

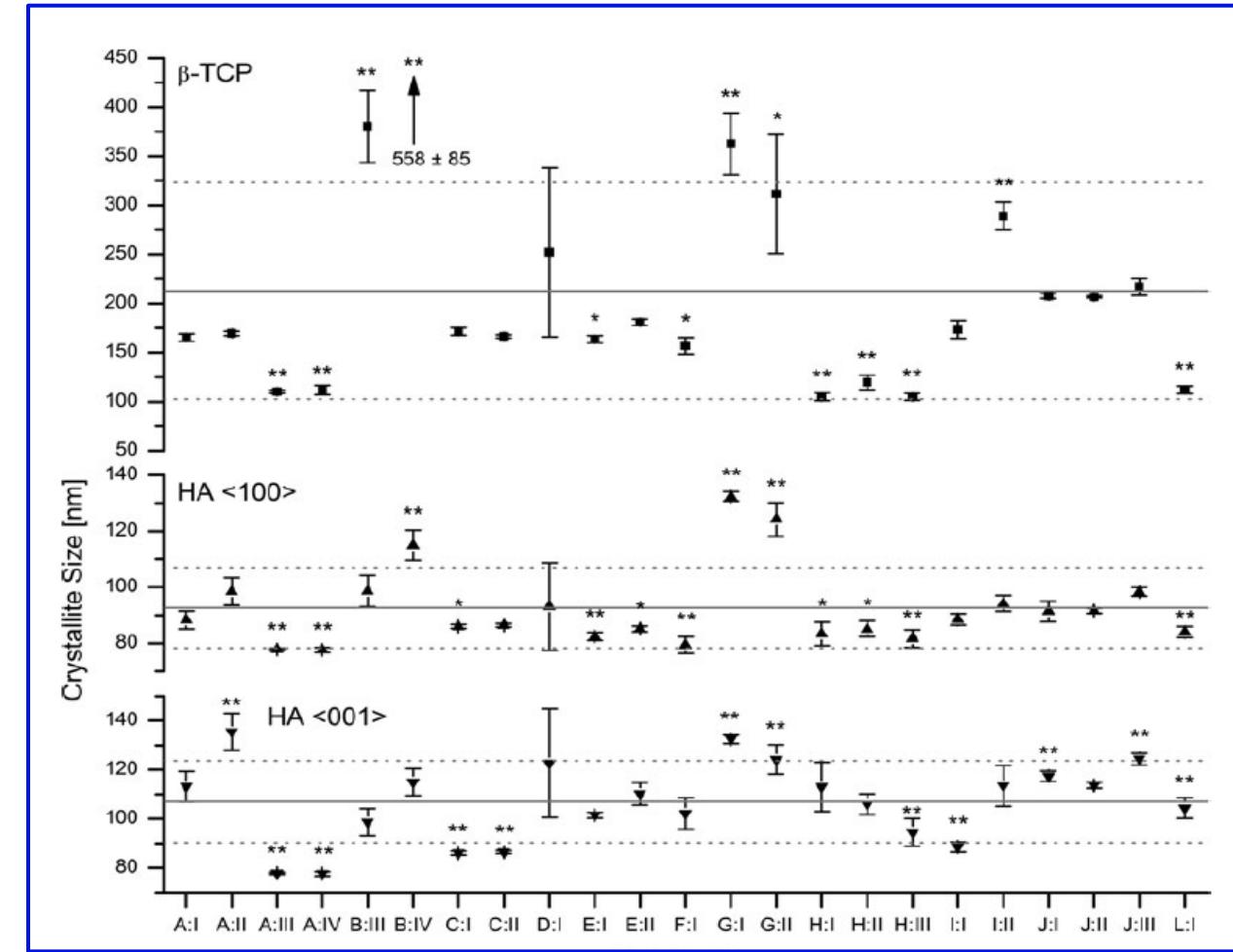


PSI

# X-ray diffraction and scattering (WAXS) methods

MSE-674

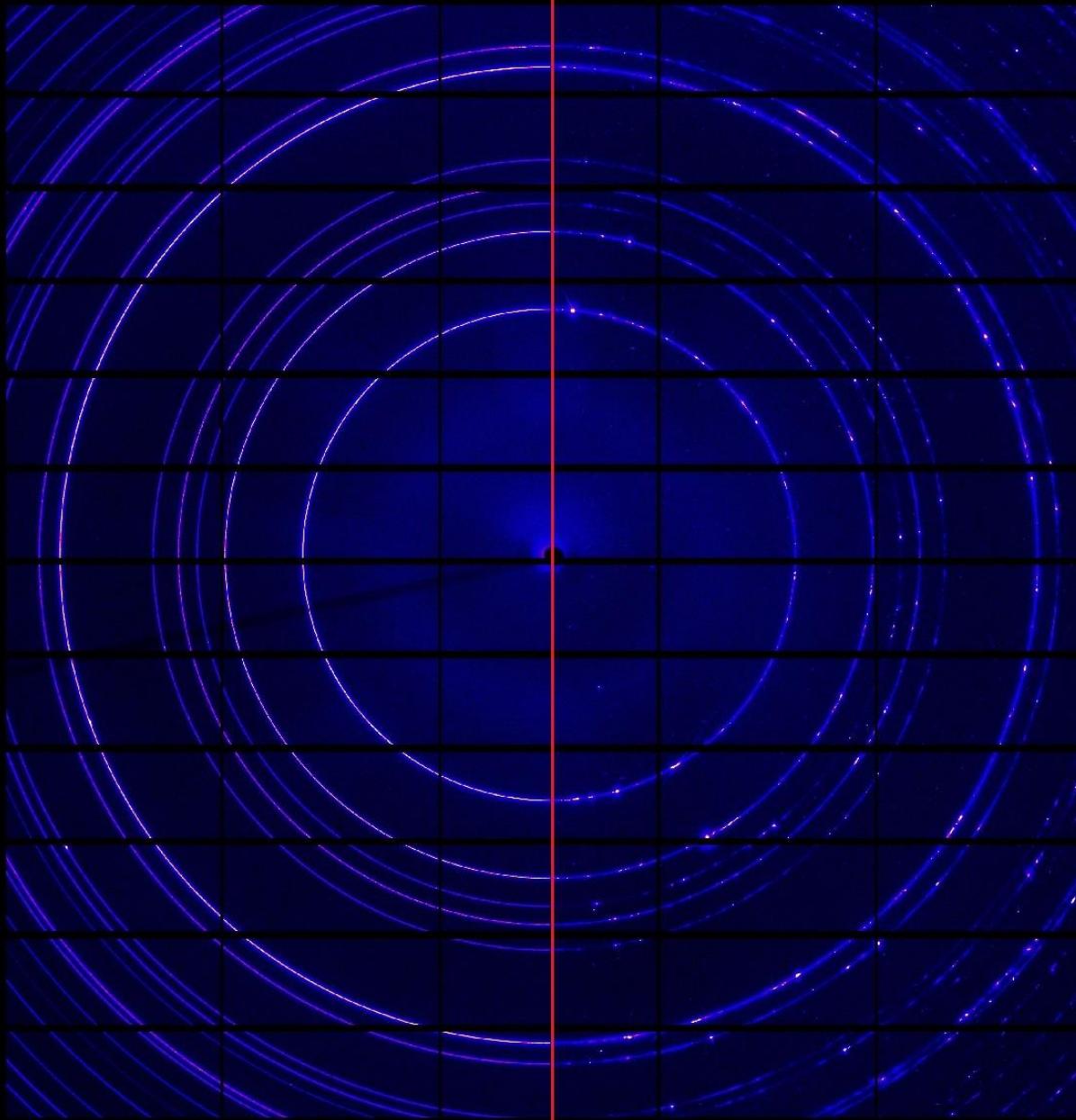
Multidisciplinary approach to NPs characterization



Nicola Casati

ADDAMS beamline, Advanced DiffrAction for Materials Science  
Multidisciplinary approach to NPs characterization, January 2025

# Outline



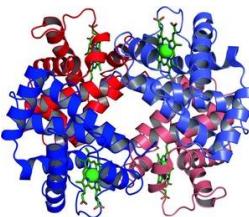
- Brief recap of XRD
- Instrumentation
- **Size & Strain**
- Some advanced stuff
- What's a Refinement?
- Play time

# Diffraction for materials



Where are the atoms?

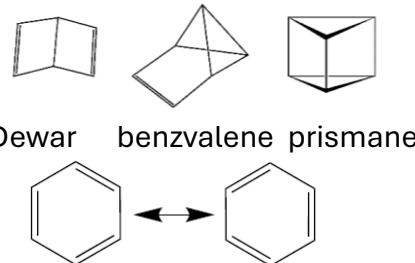
Protein structure



How are they linked?

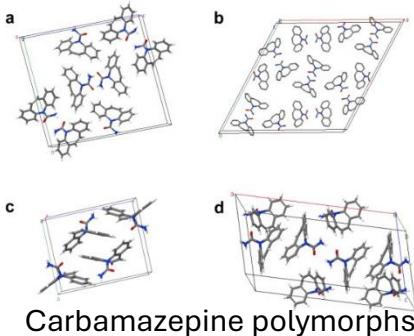
Activity

Molecules



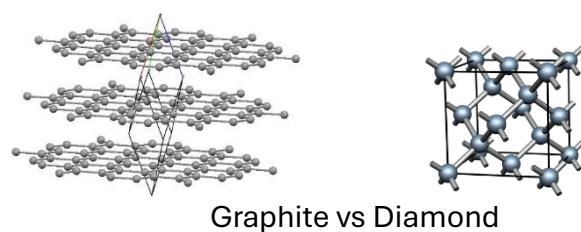
Reactivity

Pharmaceutical phases



Bioavailability

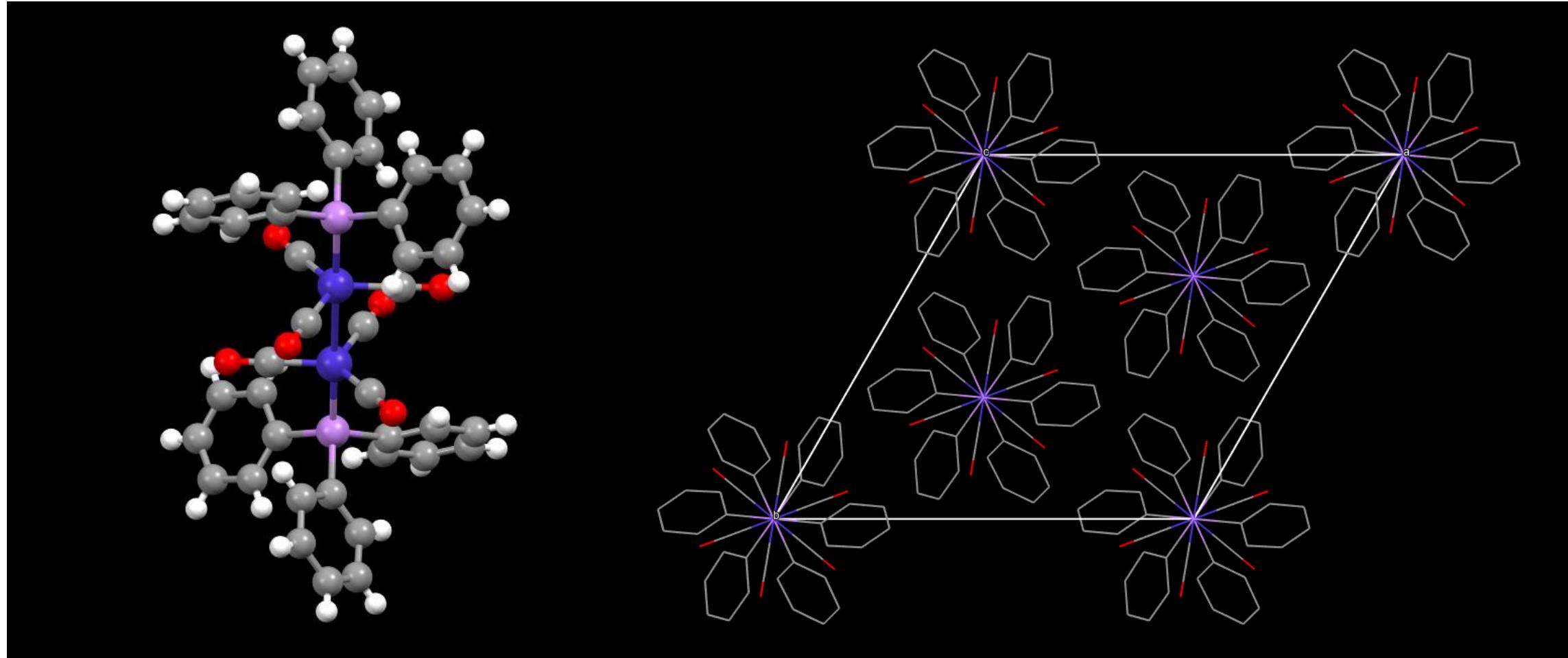
Materials



Properties

Graphite vs Diamond

# What's a crystal structure?



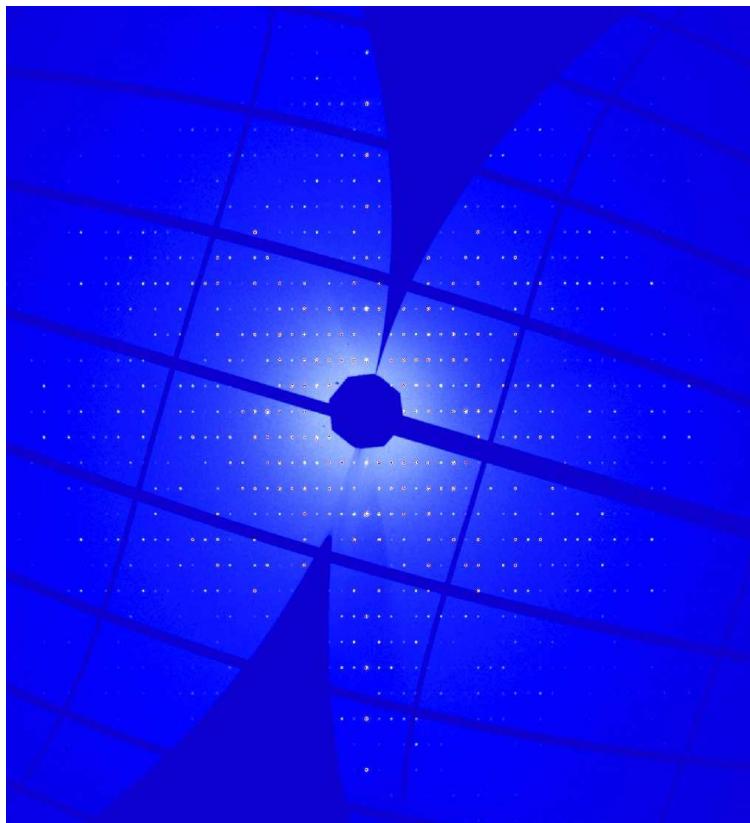
# From structure to diffraction and back

Diffraction signal



CIF

(Crystallographic Information  
File)



```
_symmetry_cell_setting      monoclinic
_symmetry_space_group_name_H-M 'P 21/n'
_symmetry_Int_Tables_number   14
_space_group_name_Hall        '-P 2yn'
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 1/2-x,1/2+y,1/2-z
3 -x,-y,-z
4 1/2+x,1/2-y,1/2+z
_cell_length_a                9.097(1)
_cell_length_b                12.764(1)
_cell_length_c                9.822(1)
_cell_angle_alpha              90
_cell_angle_beta              94.69(1)
_cell_angle_gamma              90
_cell_volume                  1136.65
_cell_formula_units_Z          4
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C -0.38703 0.00423 0.28159
C2 C -0.28602 -0.06814 0.23386
C3 C -0.19539 -0.04813 0.13133
C4 C -0.20615 0.03174 0.03190
C5 C -0.30673 0.11217 0.01310
C6 C -0.39942 0.14750 0.11176
C7 C -0.53656 0.19540 0.08539
```

# Databases and programs (just hints)

Powder Diffraction File™

<https://www.icdd.com/pdfsearch/>

Cambridge Structure Database

<http://www.ccdc.cam.ac.uk/>

Inorganic Crystal Structure Database

<http://www.fiz-karlsruhe.de/icsd.html>

Crystallography Open Database

<http://www.crystallography.net/>

PDB (Protein DataBank)

<https://www.rcsb.org/>

.... normally from single crystals (less than 1% from powders)

Topas

<http://www.topas-academic.net/>

GSAS-II

<https://advancedphotonsource.github.io/GSAS-II-tutorials/>

Fullprof

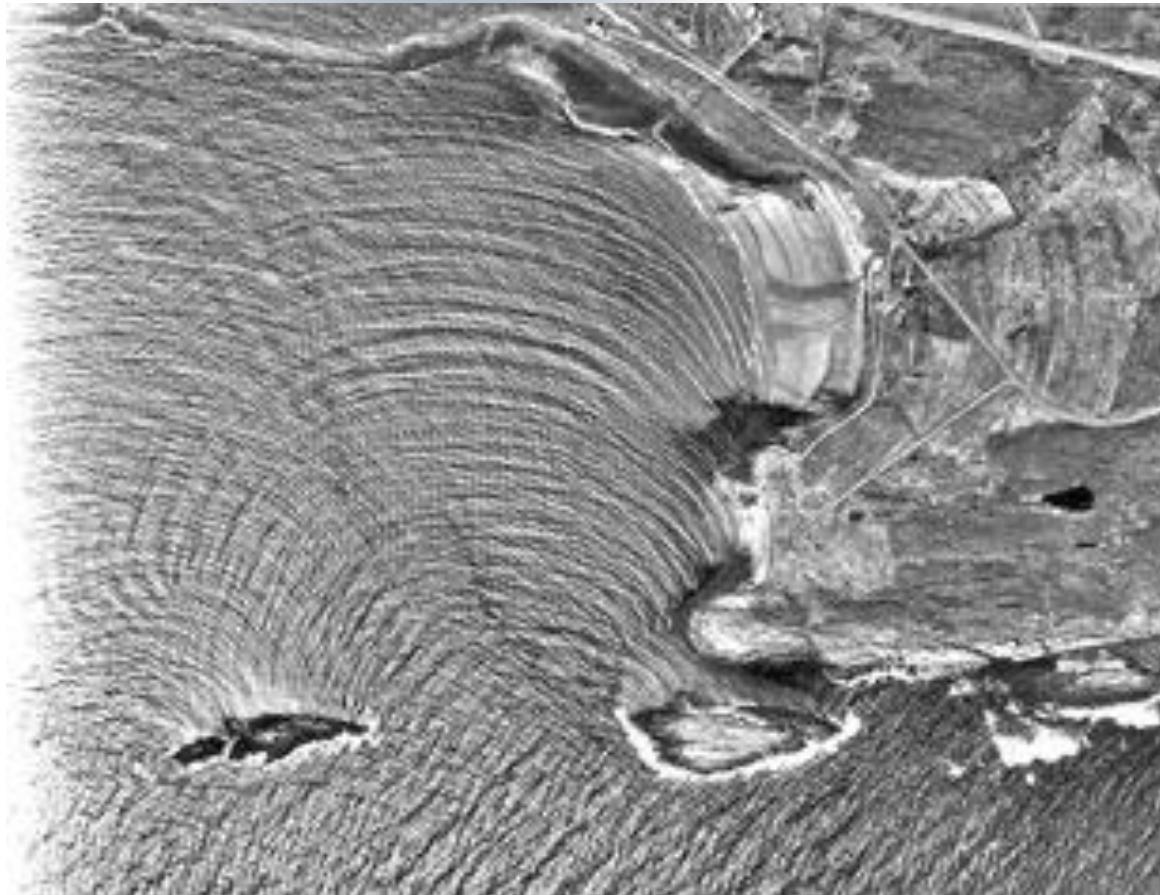
<https://www.ill.eu/sites/fullprof/>

Mercury

<https://www.ccdc.cam.ac.uk/solutions/software/free-mercury/>

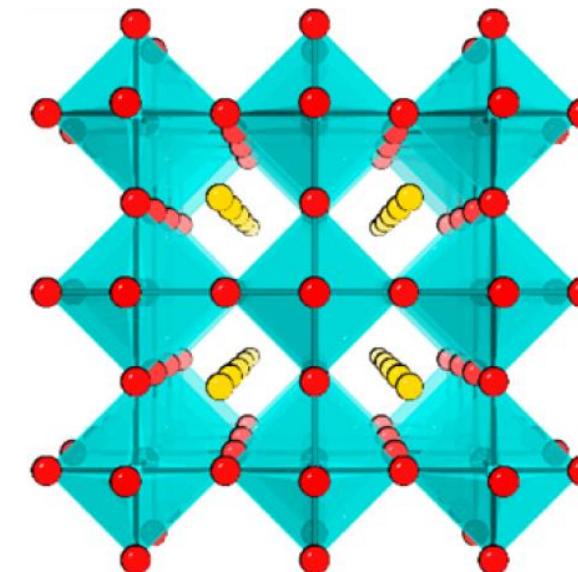
# An Interferometric method

Interferometric: using the interference between waves (light) to obtain information (typically with the same length scale of the wavelength used)

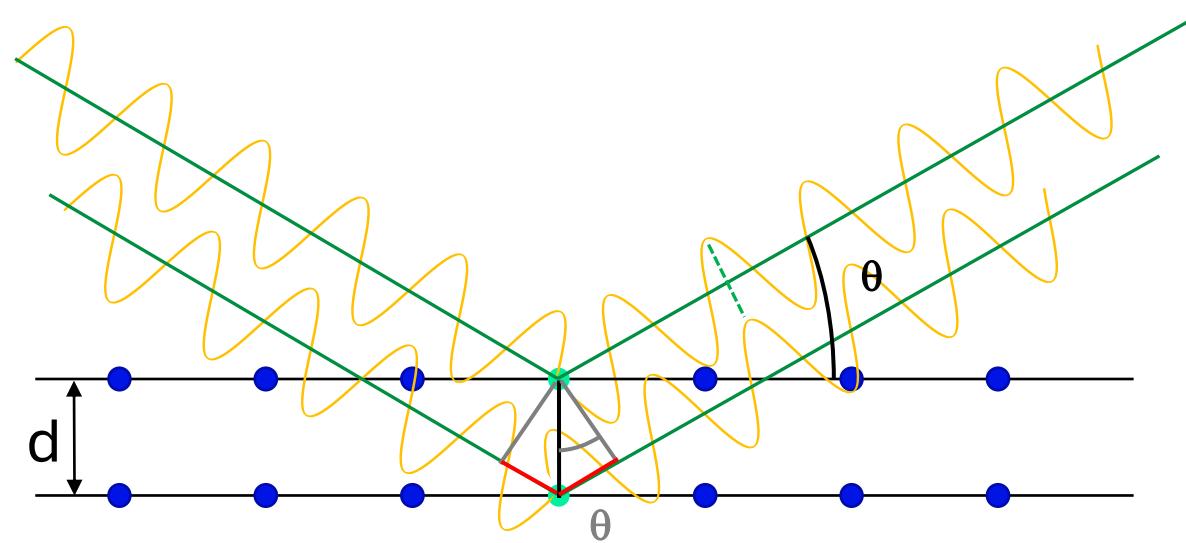


## CRYSTALS

Ordered arrangement of atoms with periodic repetition in all directions  
(3D grating)



# Scattering from a crystal

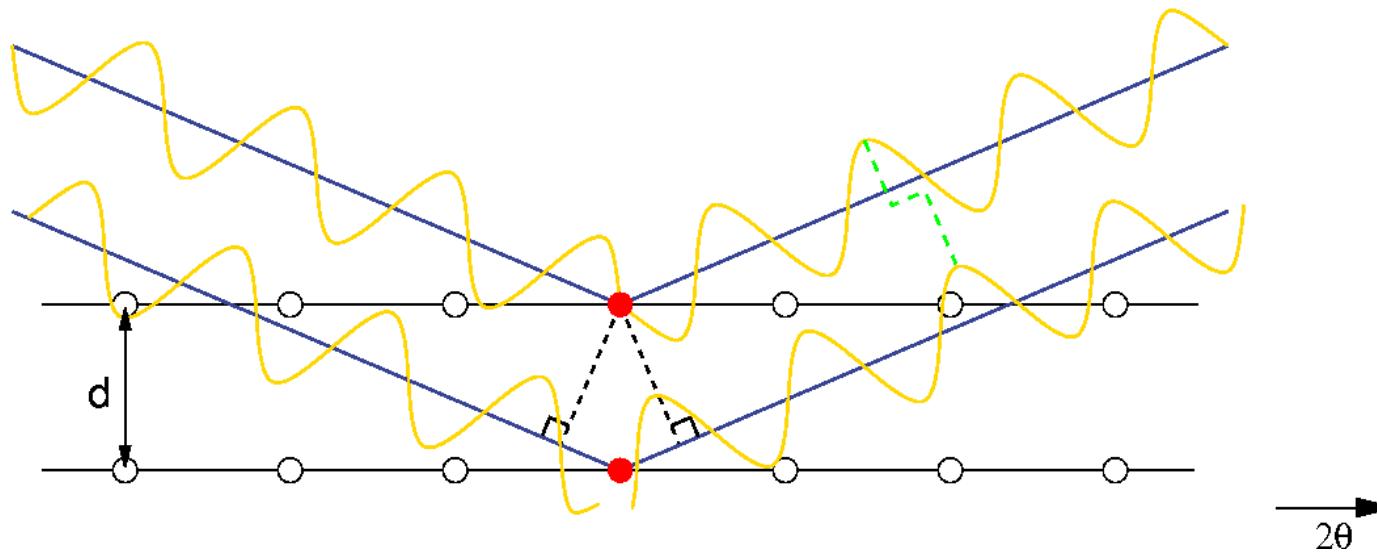


$$n\lambda = 2d \sin(\theta) \quad \text{Bragg's law}$$

- What are the dots that scatter elastically the X-rays in crystals?
- X-rays are electromagnetic waves and they interact primarily with **electrons** (clouds)
- Different elements possess different Z, so scatter more or less strongly

# That equation ...

© PRW



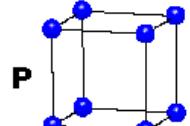
$$m\lambda = 2d \sin \theta$$

$$\theta \text{ nis } \frac{m\lambda}{2d}$$

# Indexing, Bravais lattice

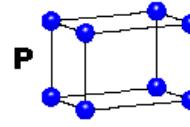
## CUBIC

$a = b = c$   
 $\alpha = \beta = \gamma = 90^\circ$



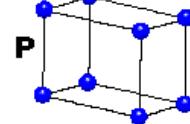
## TETRAGONAL

$a = b \neq c$   
 $\alpha = \beta = \gamma = 90^\circ$



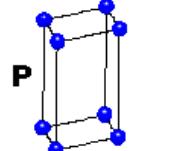
## ORTHORHOMBIC

$a \neq b \neq c$   
 $\alpha = \beta = \gamma = 90^\circ$



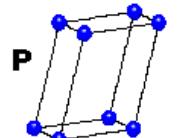
## HEXAGONAL

$a = b \neq c$   
 $\alpha = \beta = 90^\circ$   
 $\gamma = 120^\circ$



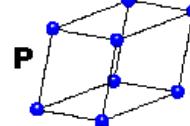
## MONOCLINIC

$a \neq b \neq c$   
 $\alpha = \gamma = 90^\circ$   
 $\beta \neq 120^\circ$

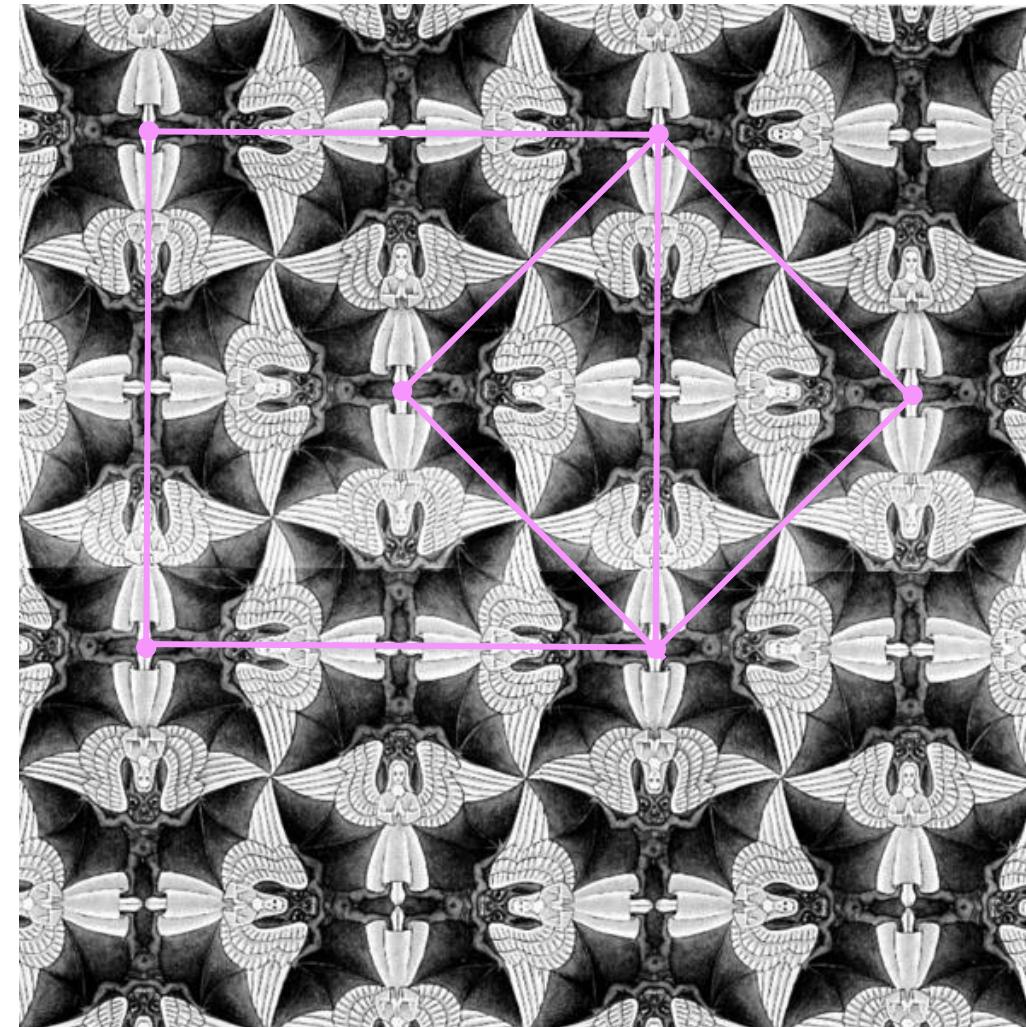


## TRICLINIC

$a \neq b \neq c$   
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$



<http://www.chm.bris.ac.uk/webprojects2003/cook/latticetypes.htm>

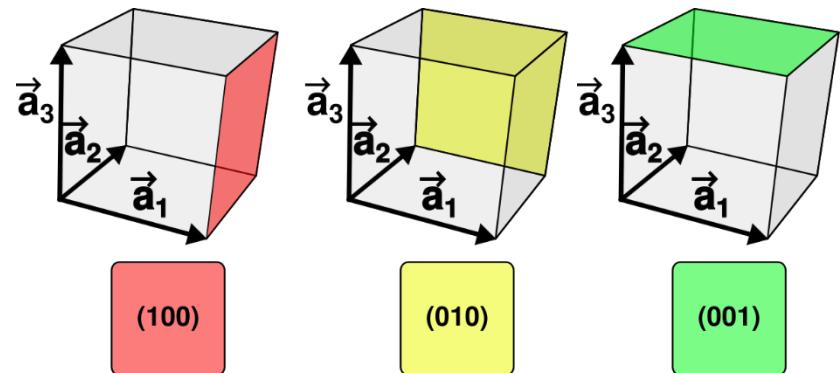


Systematic absences for extra symmetry

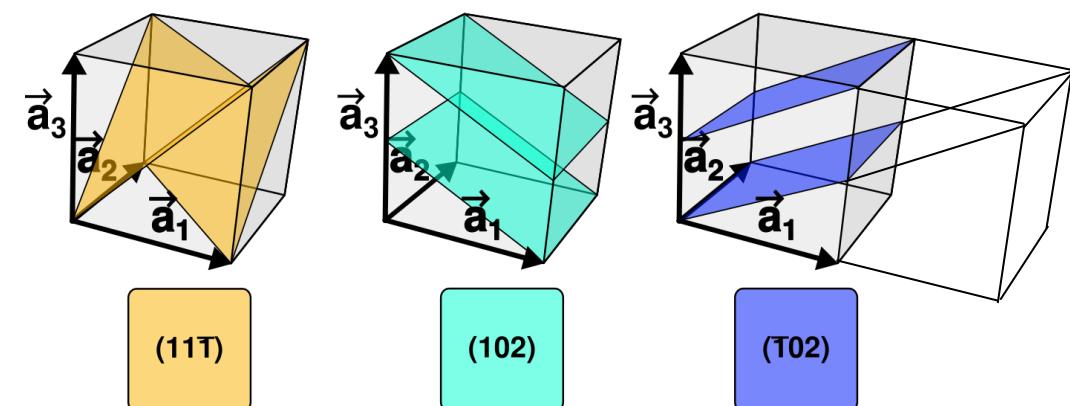
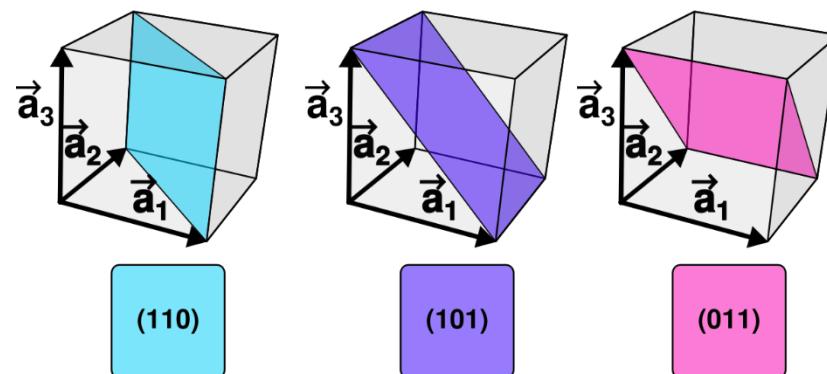
# Miller indeces (h k l)

$$n\lambda = 2d \sin(\theta)$$

Bragg's law



- What are the dots that scatter elastically the X-rays in crystals?



# Indexing

$$n\lambda = 2d \sin(\theta) \quad \text{Bragg's law}$$

Cubic	$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$
Tetragonal	$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$
Orthorhombic	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Hexagonal	$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$
Monoclinic	$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$
Triclinic	$\frac{1}{d^2} = \frac{1}{V^2} [h^2 b^2 c^2 \sin^2 \alpha + k^2 a^2 c^2 \sin^2 \beta + l^2 a^2 b^2 \sin^2 \gamma + 2h k a b c^2 (\cos \alpha \cos \beta - \cos \gamma) + 2k l a^2 b c (\cos \beta \cos \gamma - \cos \alpha) + 2h l a b^2 c (\cos \alpha \cos \gamma - \cos \beta)]$



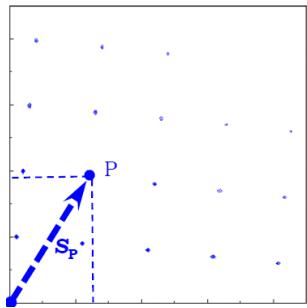
Systematic absences for extra symmetry

# Structure factor

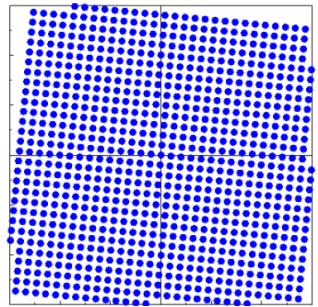
$$I_{hkl} \propto |F_{hkl}|^2$$

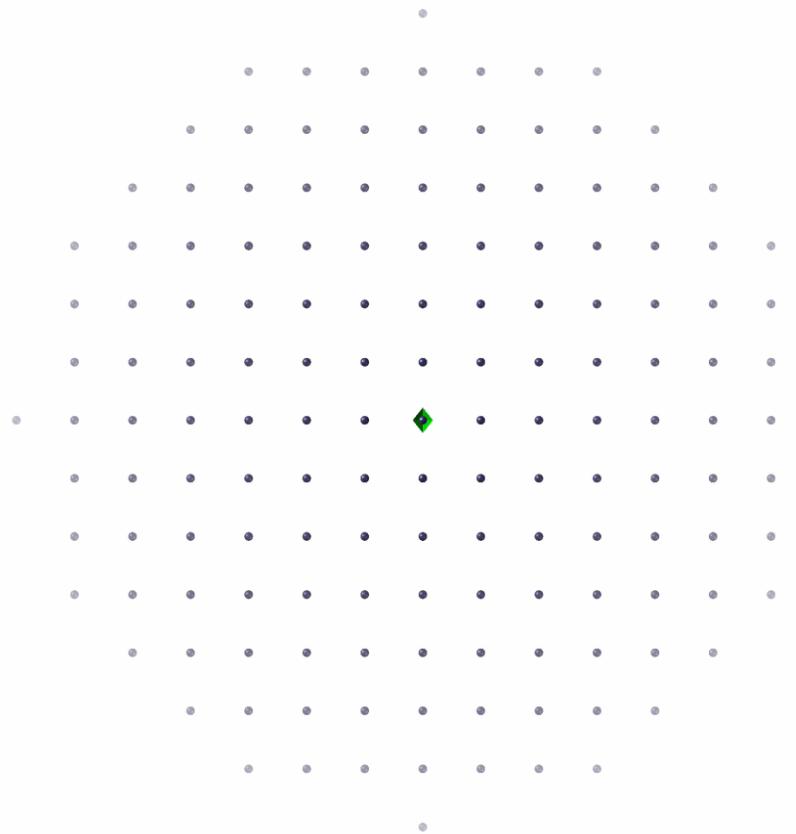
$$F_{hkl} = \sum_{j=1}^N f_j e^{[-2\pi i(hx_j + ky_j + \ell z_j)]}$$

# Powder Diffraction



Single



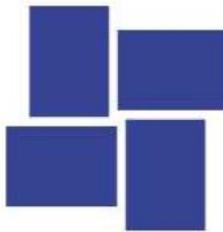


# Different objects for diffraction

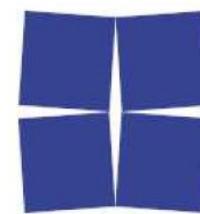
single  
crystal



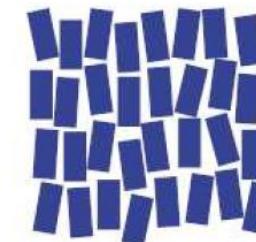
twinned  
crystal



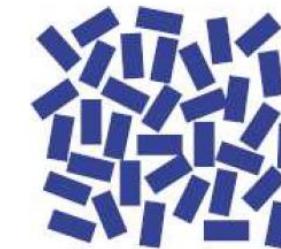
crystal with  
mosaic spread



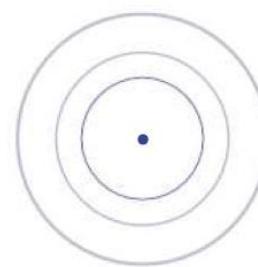
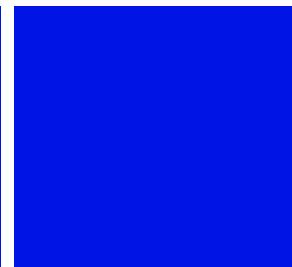
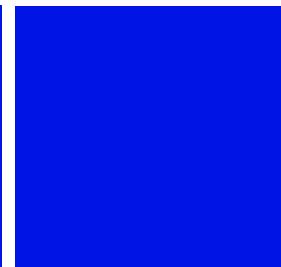
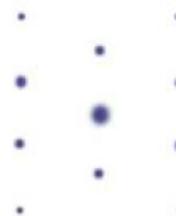
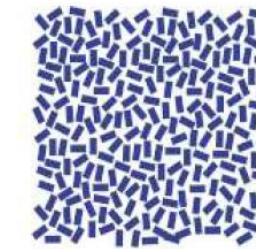
textured  
sample



powder  
sample

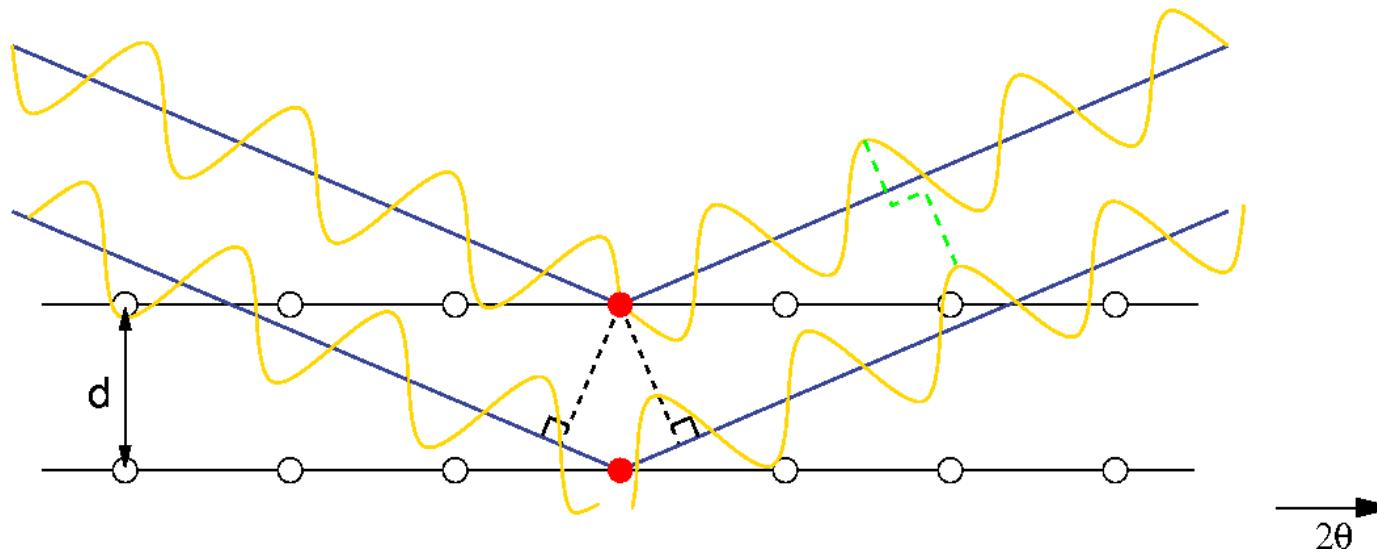


nanocrystalline  
powder



# That equation ...

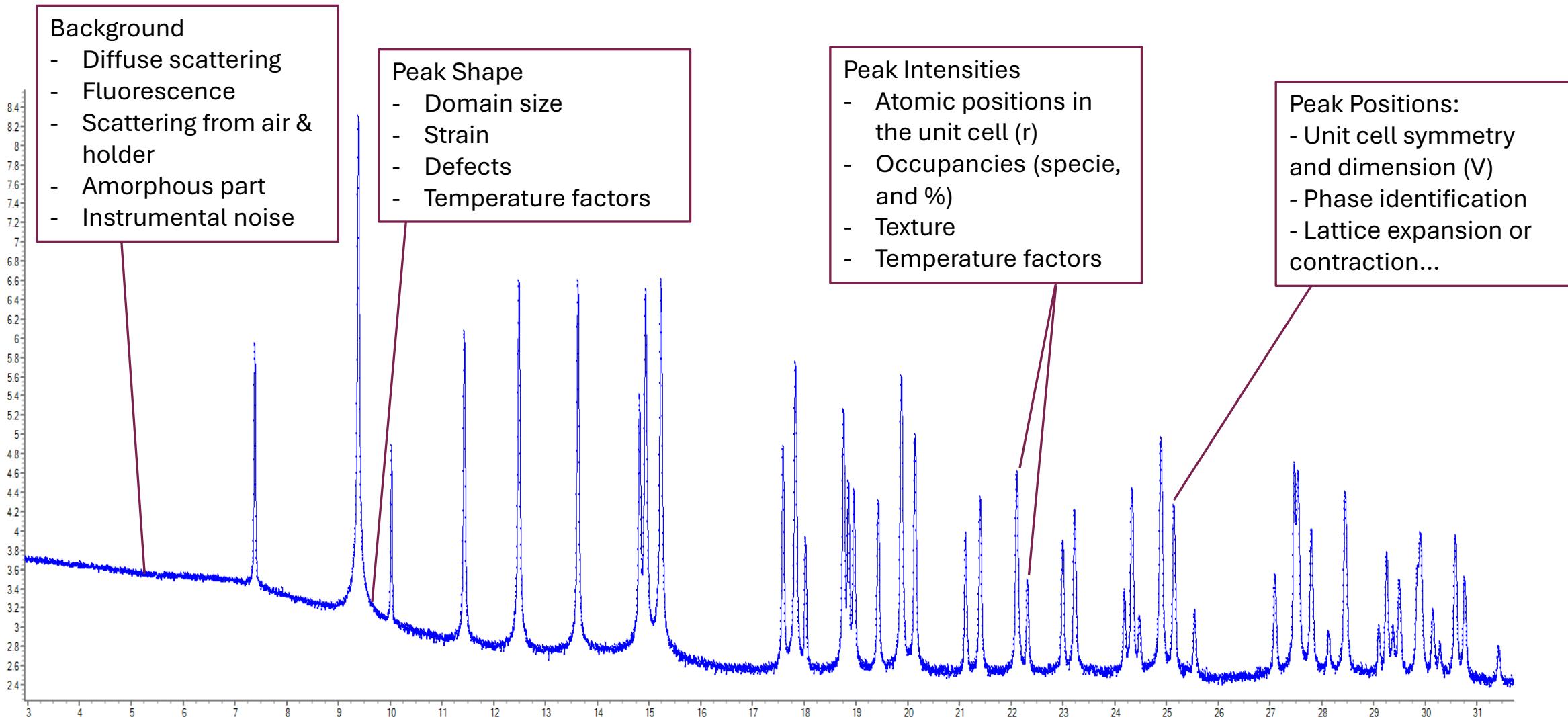
© PRW



$$m\lambda = 2d \sin \theta$$

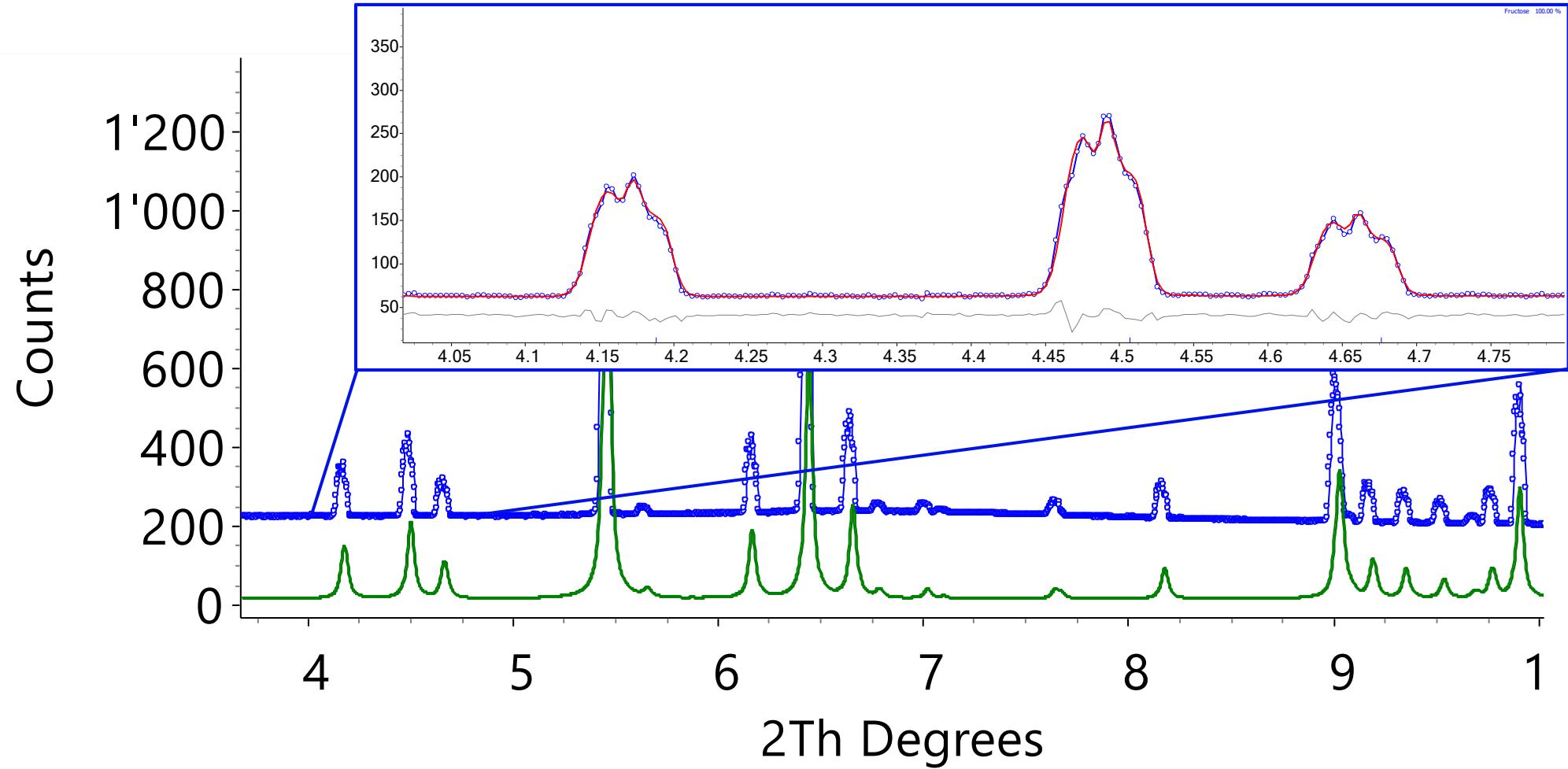
$$\theta \text{ nis } \frac{m\lambda}{2d}$$

# Diffractogram



# Peak broadening

- Instrument
- Setup
- Sample



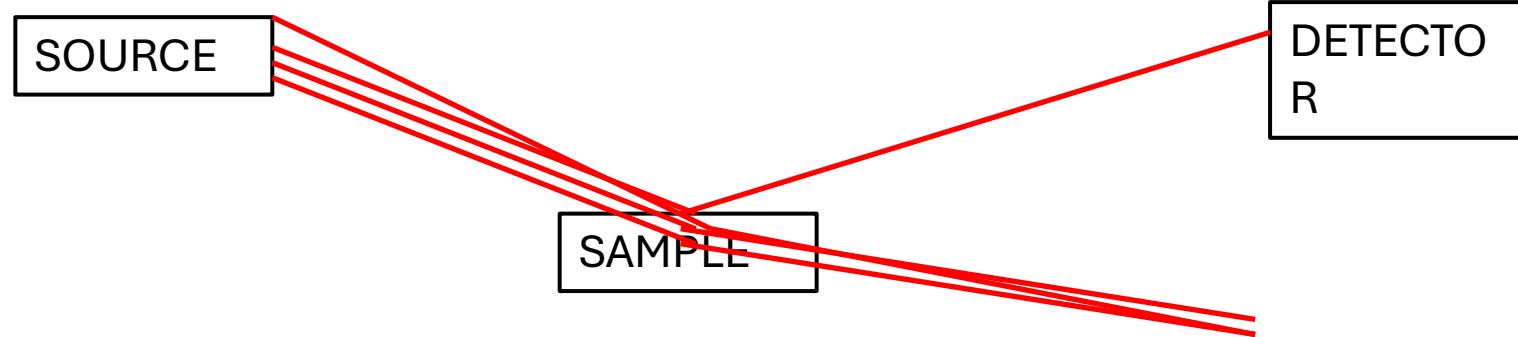
# Sample, Instrument, Measurement, Data

- Everything contributes to your data
- No measurement is ever 'perfect'
- Info you are looking for are mixed with info you do not need (or you should already know ...)
- Wrong start, wrong end!

*The better you can see  
the more the details become relevant*

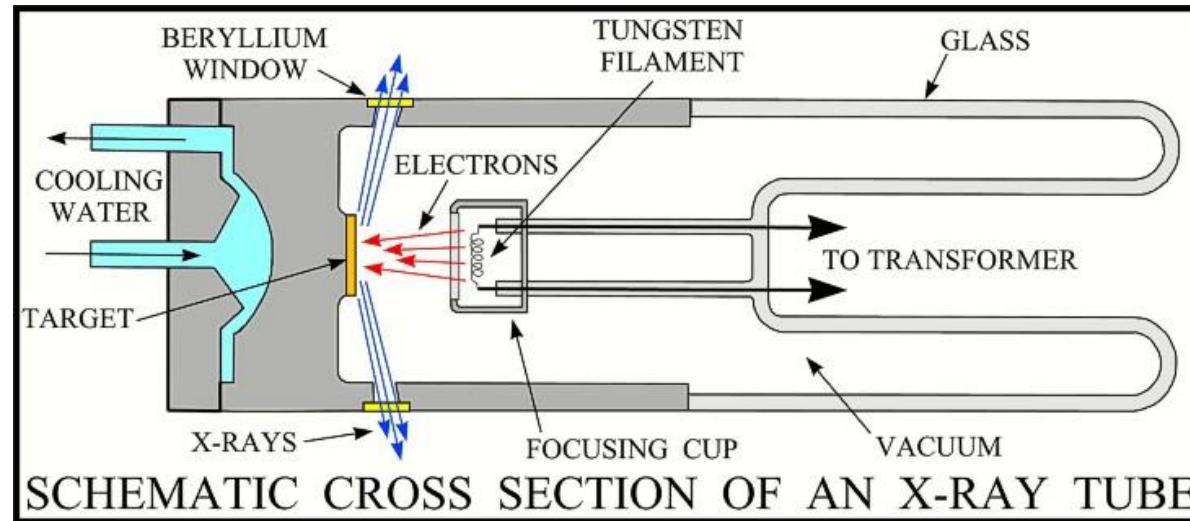


# Diffraction measurement/experiment



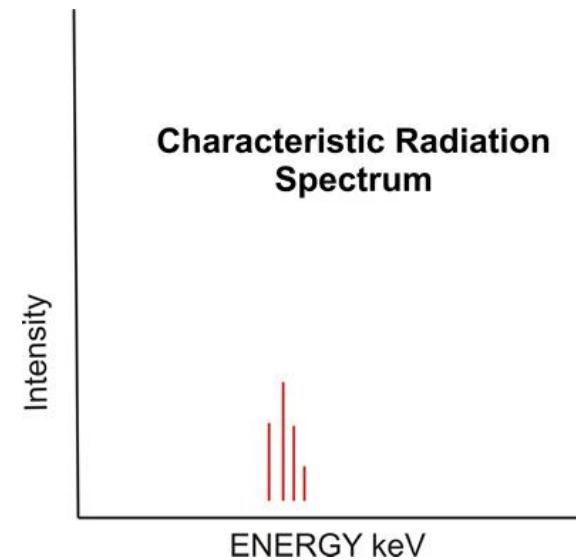
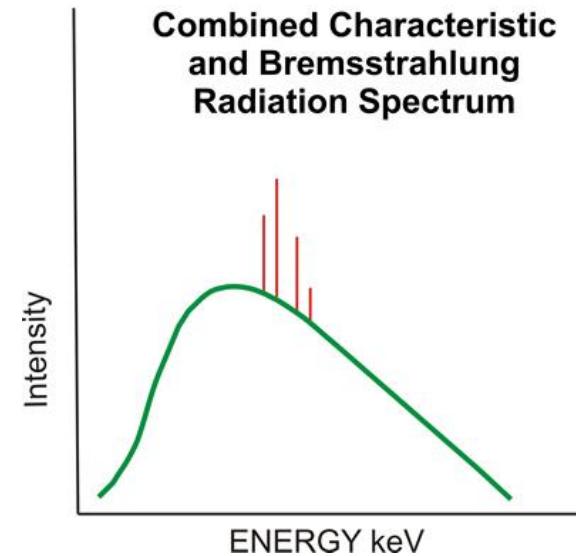
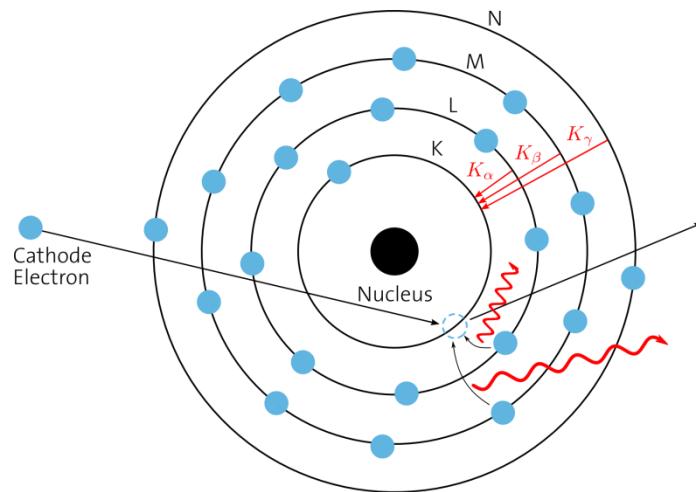
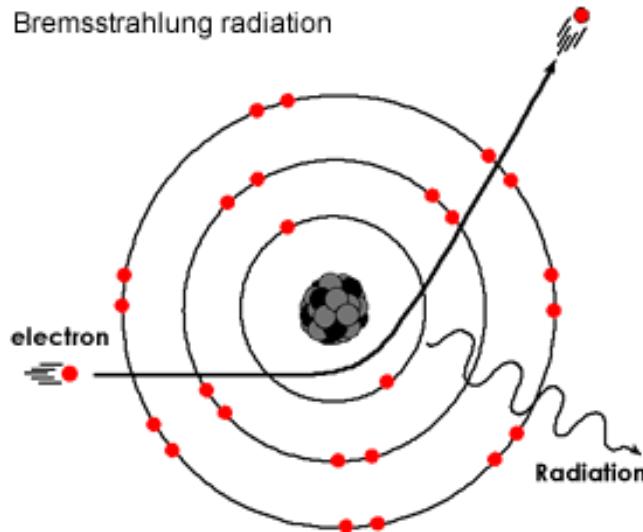
Optical elements can be used in combination to produce various setups, with different characteristics

# Source – X-ray tube



- Standard Targets: Cu/Mo/Ag

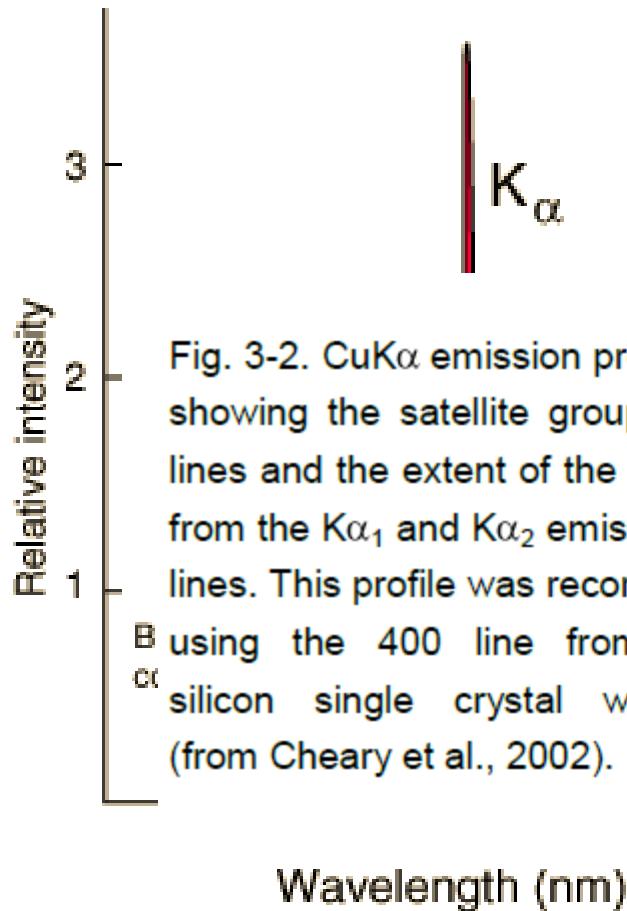
# Source – X-ray tube



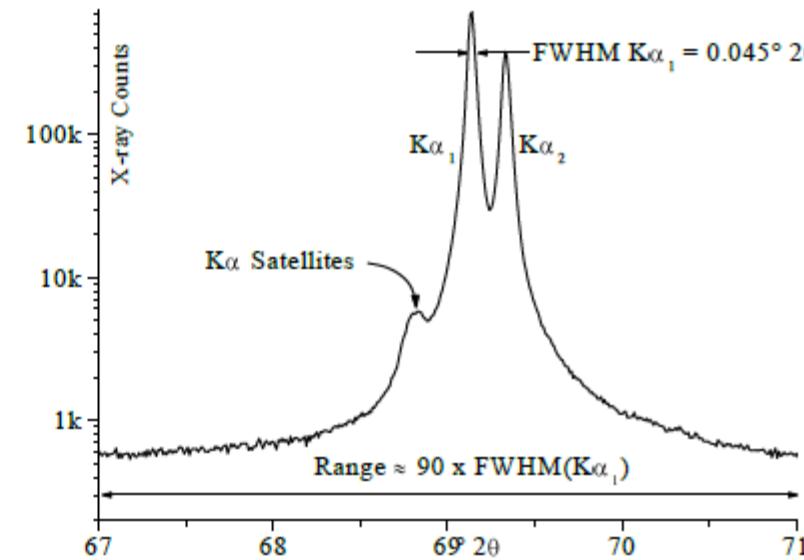
# Binding Energies

Symbol	Z
name	
H hydrog	14
Li lithium	3
Na sodium	11
Mg magnesium	12
Al aluminum	13
Si silicon	14
P phosphorus	15
S sulfur	16
Cl chlorine	17
Ar argon	18
K potassium	19
Ca calcium	20
Sc scandium	21
Ti titanium	22
V vanadium	23
Cr chromium	24
Mn manganese	25
Kr krypton	36
Ca calcium	20
Sc scandium	21
Ti titanium	22
V vanadium	23
Cr chromium	24
Mn manganese	25
Fe iron	26
Co cobalt	27
Ni nickel	28
Cu copper	29
Zn zinc	30
Ar argon	31
K potassium	39
Ca calcium	40
Sc scandium	41
Ti titanium	42
V vanadium	43
Cr chromium	44
Mn manganese	45
Fe iron	46
Co cobalt	47
Ni nickel	48
Cu copper	49
Zn zinc	50
Ar argon	54
K potassium	55
Ca calcium	56
Sc scandium	57
Ti titanium	58
V vanadium	59
Cr chromium	60
Mn manganese	61
Fe iron	62
Co cobalt	63
Ni nickel	64
Cu copper	65
Zn zinc	66
Ar argon	70
K potassium	77
Ca calcium	78
Sc scandium	79
Ti titanium	80
V vanadium	81
Cr chromium	82
Mn manganese	83
Fe iron	84
Co cobalt	85
Ni nickel	86
Cu copper	87
Zn zinc	88
Ar argon	90
K potassium	91
Ca calcium	92
Sc scandium	93
Ti titanium	94
V vanadium	95
Cr chromium	96
Mn manganese	97
Fe iron	98
Co cobalt	99
Ni nickel	100
Cu copper	101
Zn zinc	102
Ar argon	103
K potassium	104
Ca calcium	105
Sc scandium	106
Ti titanium	107
V vanadium	108
Cr chromium	109
Mn manganese	110
Fe iron	111
Co cobalt	112
Ni nickel	113
Cu copper	114
Zn zinc	115
Ar argon	116
K potassium	117
Ca calcium	118
Sc scandium	119
Ti titanium	120
V vanadium	121
Cr chromium	122
Mn manganese	123
Fe iron	124
Co cobalt	125
Ni nickel	126
Cu copper	127
Zn zinc	128
Ar argon	129
K potassium	130
Ca calcium	131
Sc scandium	132
Ti titanium	133
V vanadium	134
Cr chromium	135
Mn manganese	136
Fe iron	137
Co cobalt	138
Ni nickel	139
Cu copper	140
Zn zinc	141
Ar argon	142
K potassium	143
Ca calcium	144
Sc scandium	145
Ti titanium	146
V vanadium	147
Cr chromium	148
Mn manganese	149
Fe iron	150
Co cobalt	151
Ni nickel	152
Cu copper	153
Zn zinc	154
Ar argon	155
K potassium	156
Ca calcium	157
Sc scandium	158
Ti titanium	159
V vanadium	160
Cr chromium	161
Mn manganese	162
Fe iron	163
Co cobalt	164
Ni nickel	165
Cu copper	166
Zn zinc	167
Ar argon	168
K potassium	169
Ca calcium	170
Sc scandium	171
Ti titanium	172
V vanadium	173
Cr chromium	174
Mn manganese	175
Fe iron	176
Co cobalt	177
Ni nickel	178
Cu copper	179
Zn zinc	180
Ar argon	181
K potassium	182
Ca calcium	183
Sc scandium	184
Ti titanium	185
V vanadium	186
Cr chromium	187
Mn manganese	188
Fe iron	189
Co cobalt	190
Ni nickel	191
Cu copper	192
Zn zinc	193
Ar argon	194
K potassium	195
Ca calcium	196
Sc scandium	197
Ti titanium	198
V vanadium	199
Cr chromium	200
Mn manganese	201
Fe iron	202
Co cobalt	203
Ni nickel	204
Cu copper	205
Zn zinc	206
Ar argon	207
K potassium	208
Ca calcium	209
Sc scandium	210
Ti titanium	211
V vanadium	212
Cr chromium	213
Mn manganese	214
Fe iron	215
Co cobalt	216
Ni nickel	217
Cu copper	218
Zn zinc	219
Ar argon	220
K potassium	221
Ca calcium	222
Sc scandium	223
Ti titanium	224
V vanadium	225
Cr chromium	226
Mn manganese	227
Fe iron	228
Co cobalt	229
Ni nickel	230
Cu copper	231
Zn zinc	232
Ar argon	233
K potassium	234
Ca calcium	235
Sc scandium	236
Ti titanium	237
V vanadium	238
Cr chromium	239
Mn manganese	240
Fe iron	241
Co cobalt	242
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Cu copper	244
Zn zinc	245
Ar argon	246
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Ca calcium	248
Sc scandium	249
Ti titanium	250
V vanadium	251
Cr chromium	252
Mn manganese	253
Fe iron	254
Co cobalt	255
Ni nickel	256
Cu copper	257
Zn zinc	258
Ar argon	259
K potassium	260
Ca calcium	261
Sc scandium	262
Ti titanium	263
V vanadium	264
Cr chromium	265
Mn manganese	266
Fe iron	267
Co cobalt	268
Ni nickel	269
Cu copper	270
Zn zinc	271
Ar argon	272
K potassium	273
Ca calcium	274
Sc scandium	275
Ti titanium	276
V vanadium	277
Cr chromium	278
Mn manganese	279
Fe iron	280
Co cobalt	281
Ni nickel	282
Cu copper	283
Zn zinc	284
Ar argon	285
K potassium	286
Ca calcium	287
Sc scandium	288
Ti titanium	289
V vanadium	290
Cr chromium	291
Mn manganese	292
Fe iron	293
Co cobalt	294
Ni nickel	295
Cu copper	296
Zn zinc	297
Ar argon	298
K potassium	299
Ca calcium	300
Sc scandium	301
Ti titanium	302
V vanadium	303
Cr chromium	304
Mn manganese	305
Fe iron	306
Co cobalt	307
Ni nickel	308
Cu copper	309
Zn zinc	310
Ar argon	311
K potassium	312
Ca calcium	313
Sc scandium	314
Ti titanium	315
V vanadium	316
Cr chromium	317
Mn manganese	318
Fe iron	319
Co cobalt	320
Ni nickel	321
Cu copper	322
Zn zinc	323
Ar argon	324
K potassium	325
Ca calcium	326
Sc scandium	327
Ti titanium	328
V vanadium	329
Cr chromium	330
Mn manganese	331
Fe iron	332
Co cobalt	333
Ni nickel	334
Cu copper	335
Zn zinc	336
Ar argon	337
K potassium	338
Ca calcium	339
Sc scandium	340
Ti titanium	341
V vanadium	342
Cr chromium	343
Mn manganese	344
Fe iron	345
Co cobalt	346
Ni nickel	347
Cu copper	348
Zn zinc	349
Ar argon	350
K potassium	351
Ca calcium	352
Sc scandium	353
Ti titanium	354
V vanadium	355
Cr chromium	356
Mn manganese	357
Fe iron	358
Co cobalt	359
Ni nickel	360
Cu copper	361
Zn zinc	362
Ar argon	363
K potassium	364
Ca calcium	365
Sc scandium	366
Ti titanium	367
V vanadium	368
Cr chromium	369
Mn manganese	370
Fe iron	371
Co cobalt	372
Ni nickel	373
Cu copper	374
Zn zinc	375
Ar argon	376
K potassium	377
Ca calcium	378
Sc scandium	379
Ti titanium	380
V vanadium	381
Cr chromium	382
Mn manganese	383
Fe iron	384
Co cobalt	385
Ni nickel	386
Cu copper	387
Zn zinc	388
Ar argon	389
K potassium	390
Ca calcium	391
Sc scandium	392
Ti titanium	393
V vanadium	394
Cr chromium	395
Mn manganese	396
Fe iron	397
Co cobalt	398
Ni nickel	399
Cu copper	400
Zn zinc	401
Ar argon	402
K potassium	403
Ca calcium	404
Sc scandium	405
Ti titanium	406
V vanadium	407
Cr chromium	408
Mn manganese	409
Fe iron	410
Co cobalt	411
Ni nickel	412
Cu copper	413
Zn zinc	414
Ar argon	415
K potassium	416
Ca calcium	417
Sc scandium	418
Ti titanium	419
V vanadium	420
Cr chromium	421
Mn manganese	422
Fe iron	423
Co cobalt	424
Ni nickel	425
Cu copper	426
Zn zinc	427
Ar argon	428
K potassium	429
Ca calcium	430
Sc scandium	431
Ti titanium	432
V vanadium	433
Cr chromium	434
Mn manganese	435
Fe iron	436
Co cobalt	437
Ni nickel	438
Cu copper	439
Zn zinc	440
Ar argon	441
K potassium	442
Ca calcium	443
Sc scandium	444
Ti titanium	445
V vanadium	446
Cr chromium	447
Mn manganese	448
Fe iron	449
Co cobalt	450
Ni nickel	451
Cu copper	452
Zn zinc	453
Ar argon	454
K potassium	455
Ca calcium	456
Sc scandium	457
Ti titanium	458
V vanadium	459
Cr chromium	460
Mn manganese	461
Fe iron	462
Co cobalt	463
Ni nickel	464
Cu copper	465
Zn zinc	466
Ar argon	467
K potassium	468
Ca calcium	469
Sc scandium	470
Ti titanium	471
V vanadium	472
Cr chromium	473
Mn manganese	474
Fe iron	475
Co cobalt	476
Ni nickel	477
Cu copper	478
Zn zinc	479
Ar argon	480
K potassium	481
Ca calcium	482
Sc scandium	483
Ti titanium	484
V vanadium	485
Cr chromium	486
Mn manganese	487
Fe iron	488
Co cobalt	489
Ni nickel	490
Cu copper	491
Zn zinc	492
Ar argon	493
K potassium	494
Ca calcium	495
Sc scandium	496
Ti titanium	497
V vanadium	498
Cr chromium	499
Mn manganese	500
Fe iron	501
Co cobalt	502
Ni nickel	503
Cu copper	504
Zn zinc	505
Ar argon	506
K potassium	507
Ca calcium	508
Sc scandium	509
Ti titanium	510
V vanadium	511
Cr chromium	512
Mn manganese	513
Fe iron	514
Co cobalt	515
Ni nickel	516
Cu copper	517
Zn zinc	518
Ar argon	519
K potassium	520
Ca calcium	521
Sc scandium	522
Ti titanium	523
V vanadium	524
Cr chromium	525
Mn manganese	526
Fe iron	527
Co cobalt	528
Ni nickel	529
Cu copper	530
Zn zinc	531
Ar argon	532
K potassium	533
Ca calcium	534
Sc scandium	535
Ti titanium	536
V vanadium	537
Cr chromium	538
Mn manganese	539
Fe iron	540
Co cobalt	541
Ni nickel	542
Cu copper	543
Zn zinc	544
Ar argon	545
K potassium	546
Ca calcium	547
Sc scandium	548
Ti titanium	549
V vanadium	550
Cr chromium	551
Mn manganese	552
Fe iron	553
Co cobalt	554
Ni nickel	555
Cu copper	556
Zn zinc	557
Ar argon	558
K potassium	559
Ca calcium	560
Sc scandium	561
Ti titanium	562
V vanadium	563
Cr chromium	564
Mn manganese	565
Fe iron	566
Co cobalt	567
Ni nickel	568
Cu copper	569
Zn zinc	570
Ar argon	571
K potassium	572
Ca calcium	573
Sc scandium	574
Ti titanium	575
V vanadium	576
Cr chromium	577
Mn manganese	578
Fe iron	579
Co cobalt	580
Ni nickel	581
Cu copper	582
Zn zinc	583
Ar argon	584
K potassium	585
Ca calcium</	

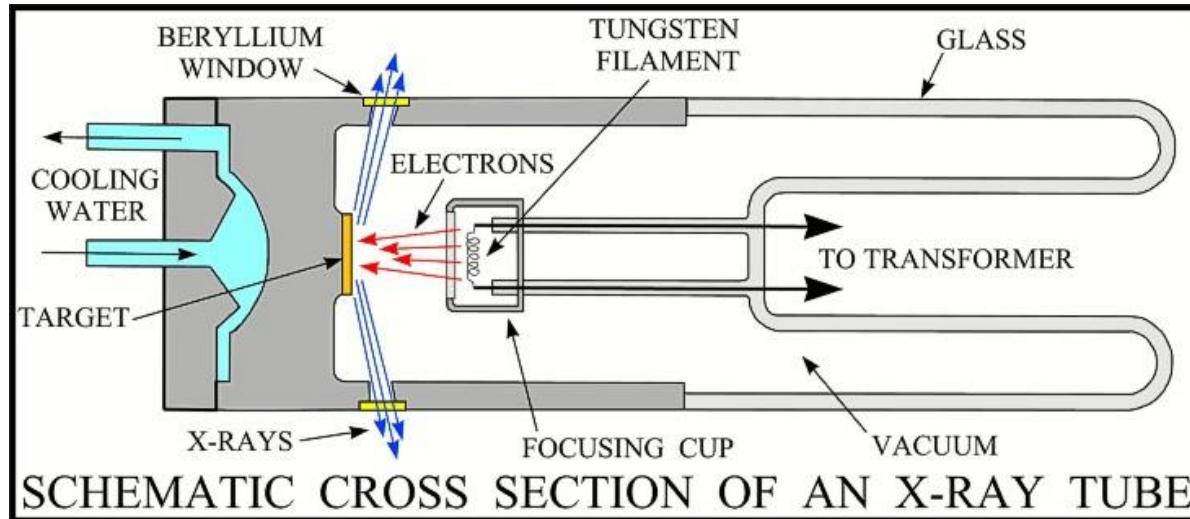
# Source – X-ray tube



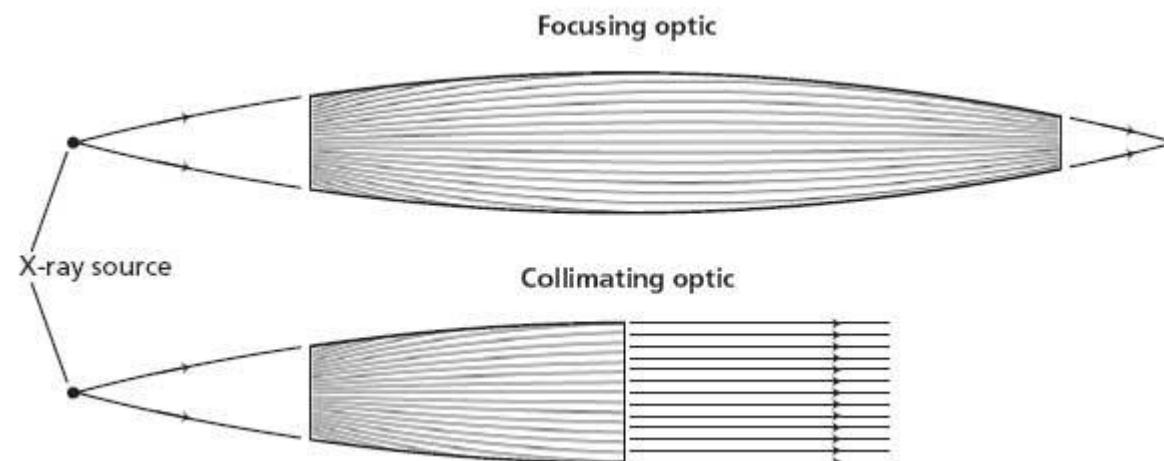
$$\lambda = 12.39842 / E(\text{keV})$$



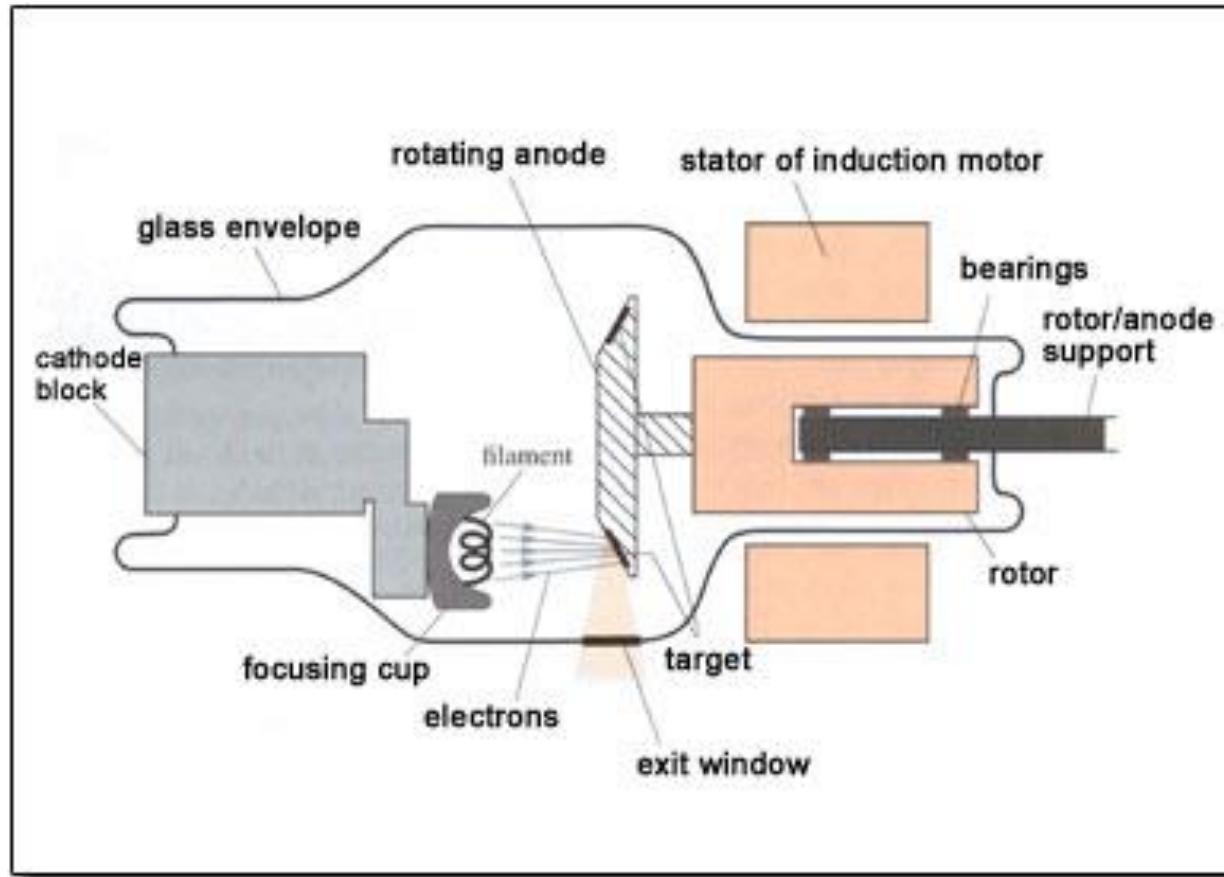
# Source – X-ray tube



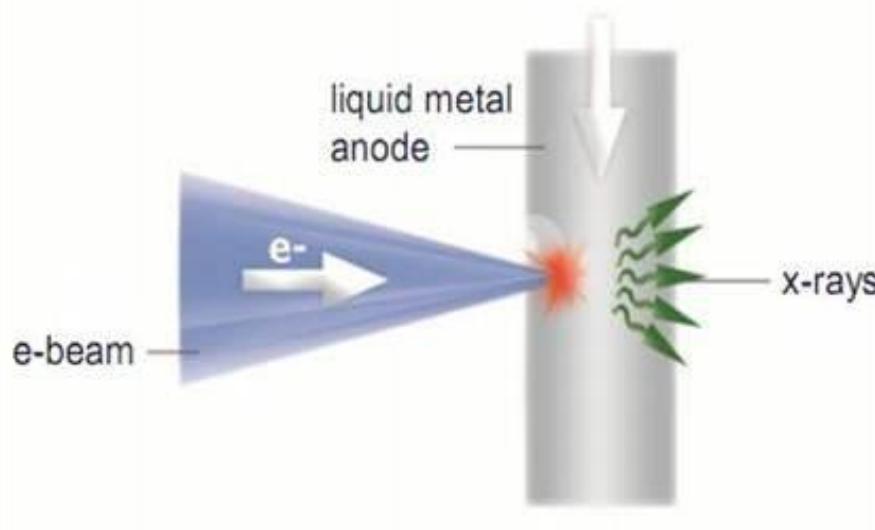
- Several kV and mA,  
several kW/mm<sup>2</sup>



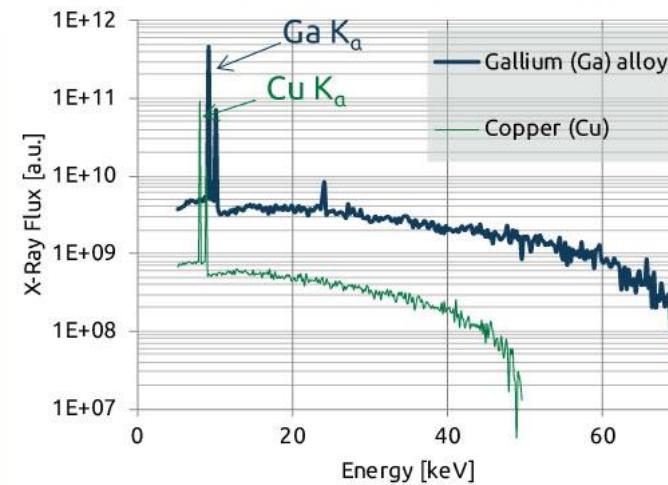
# Rotating anode



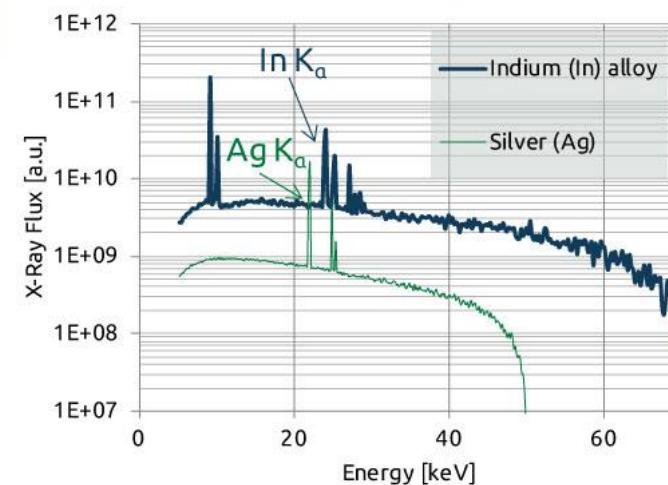
# Liquid jet



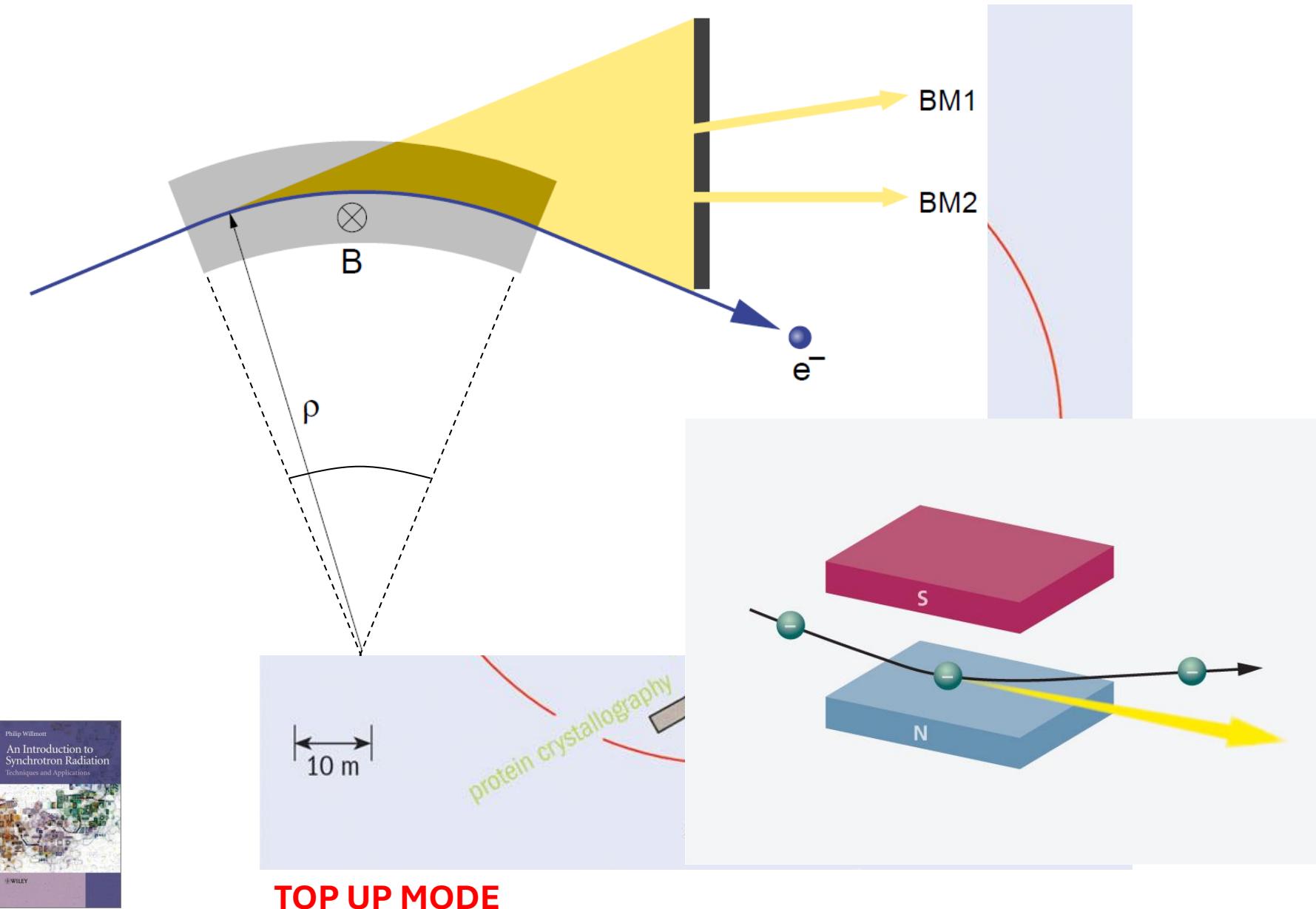
Spectra of gallium alloy and copper



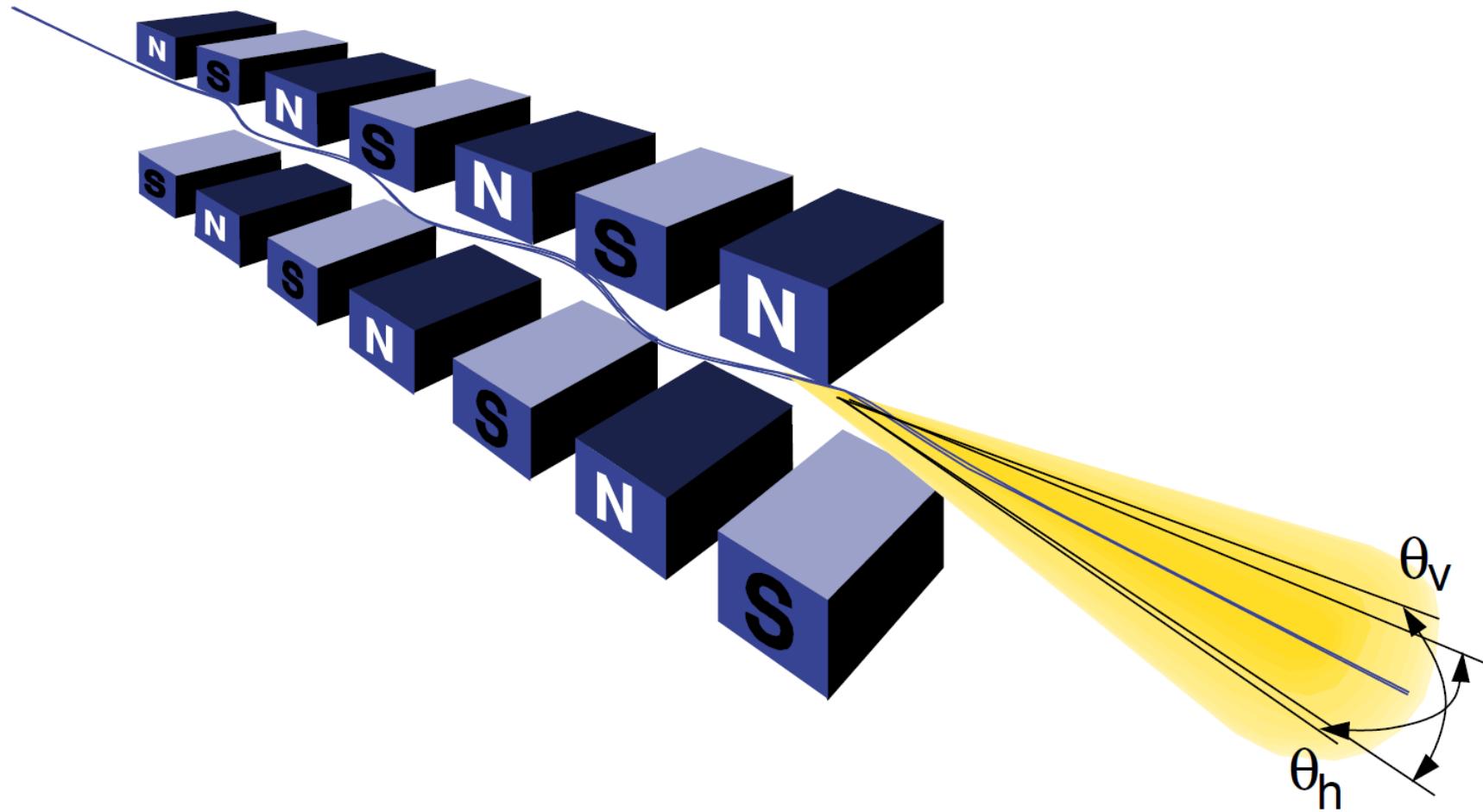
Spectra of indium alloy and silver



# Synchrotron – bending the electrons

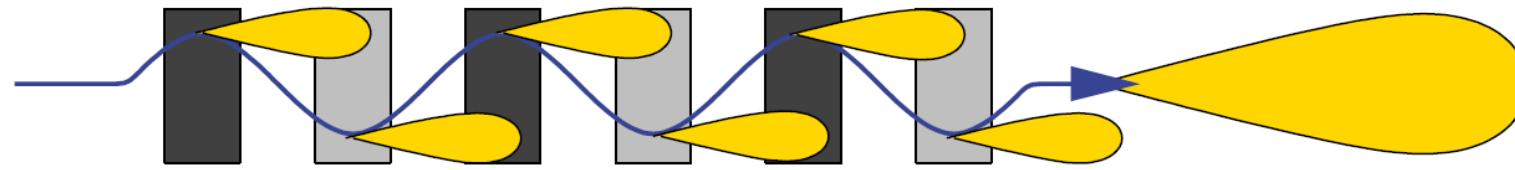


# Insertion devices

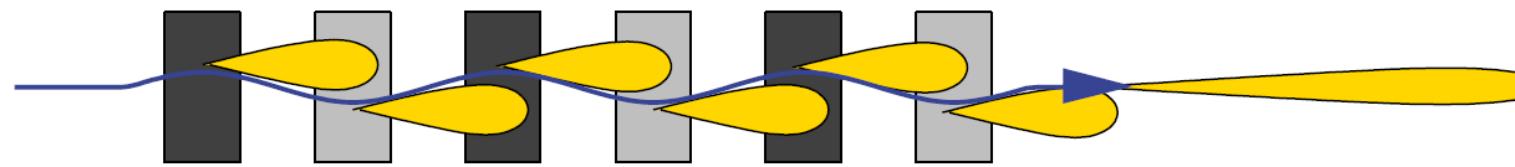


# Insertion devices

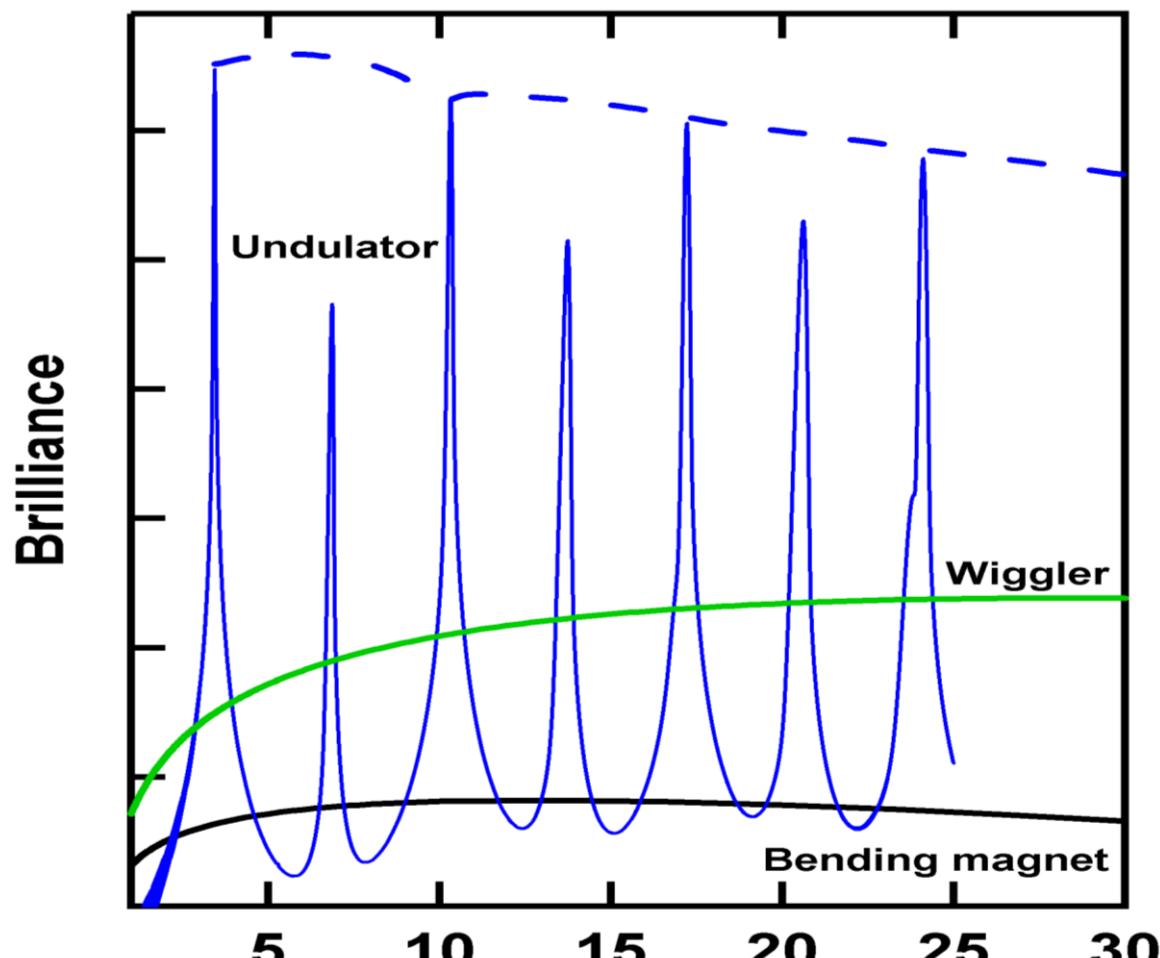
(a) Wiggler



(b) Undulator



# Insertion devices

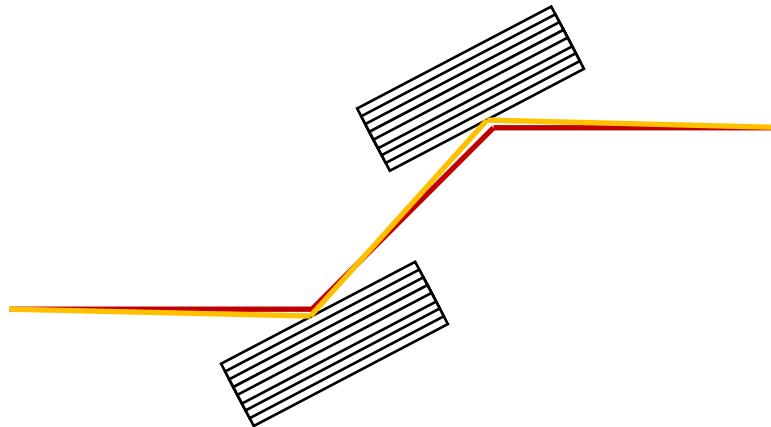


Photon Energy [keV]  $\lambda = 12.39842 / E(\text{keV})$

# Monochromator

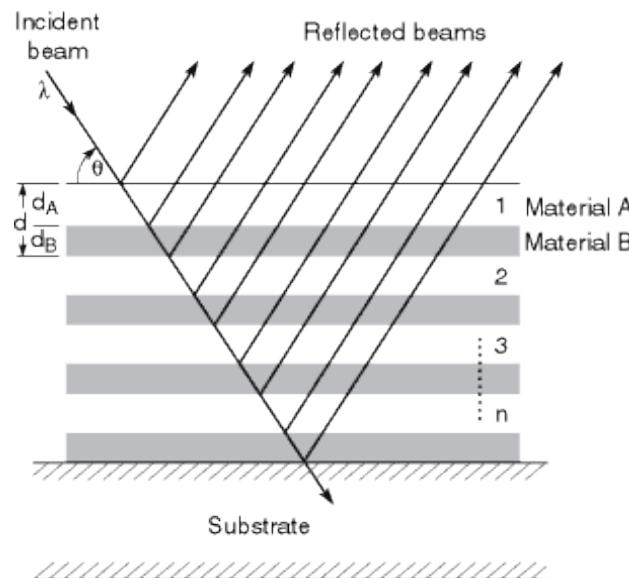
## Crystal

- $\lambda < \sim 1 \text{ nm}$

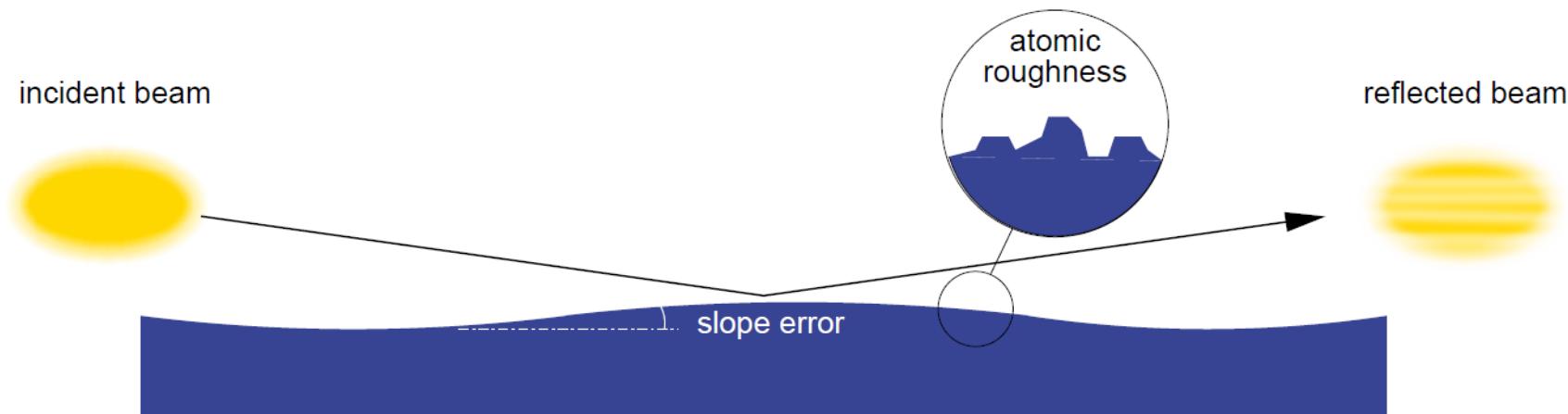
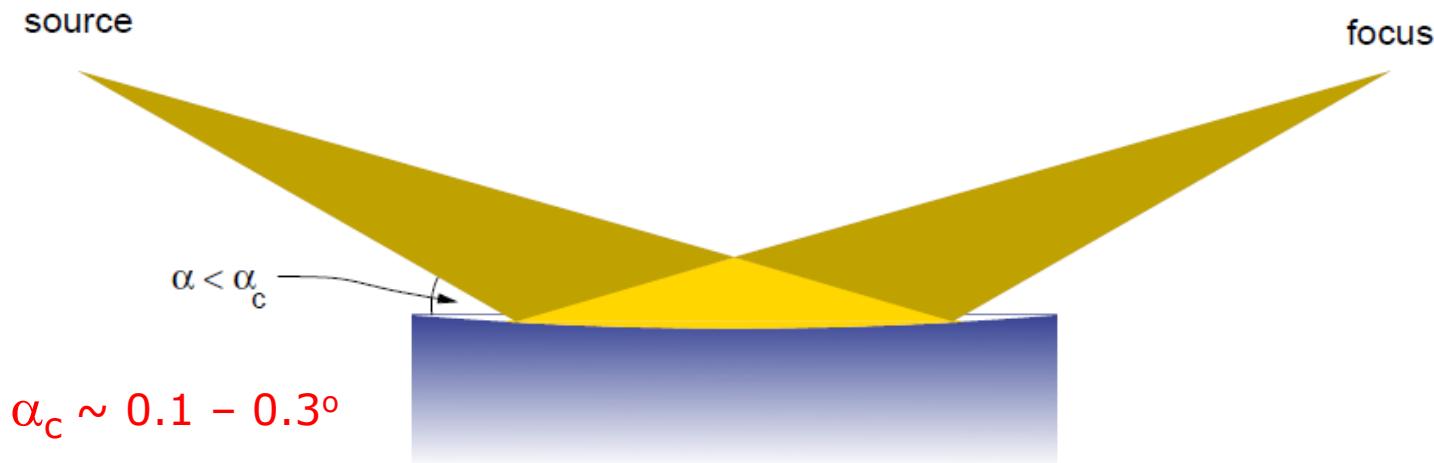


## Multilayer

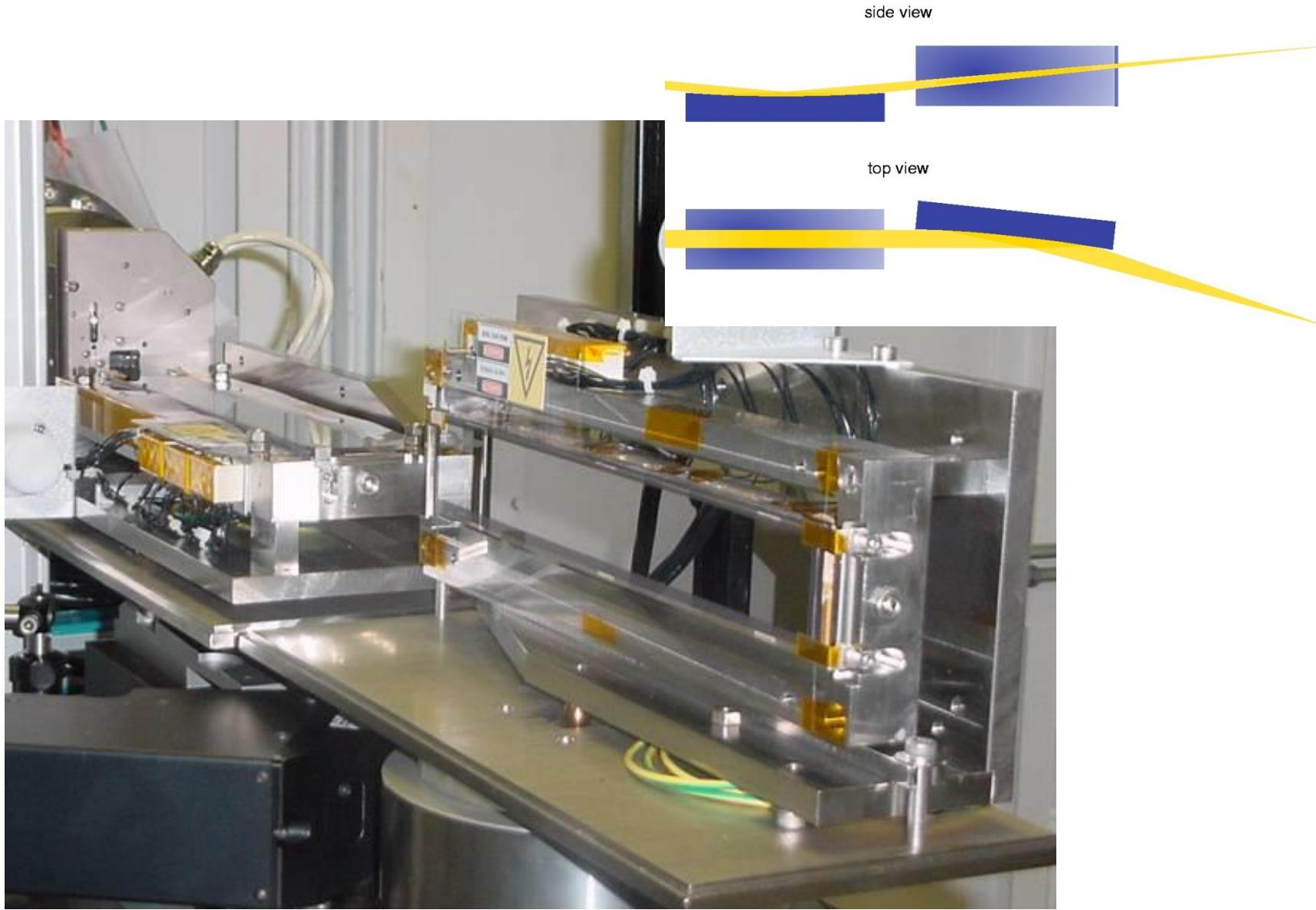
- $\Delta\lambda/\lambda$  larger (more Flux!)



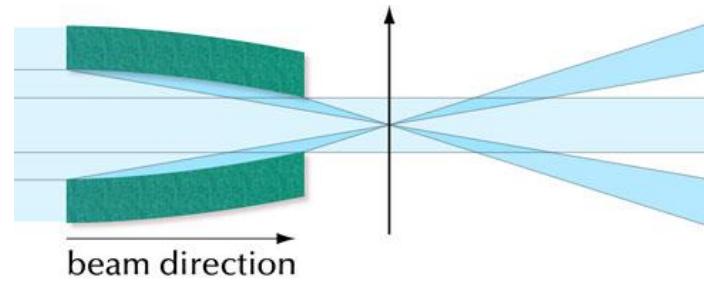
# Mirrors



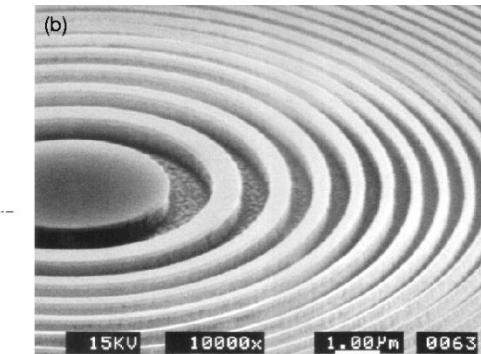
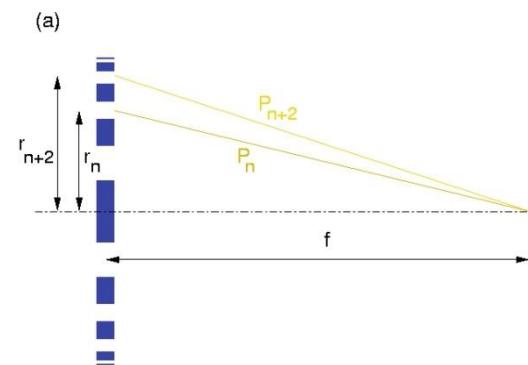
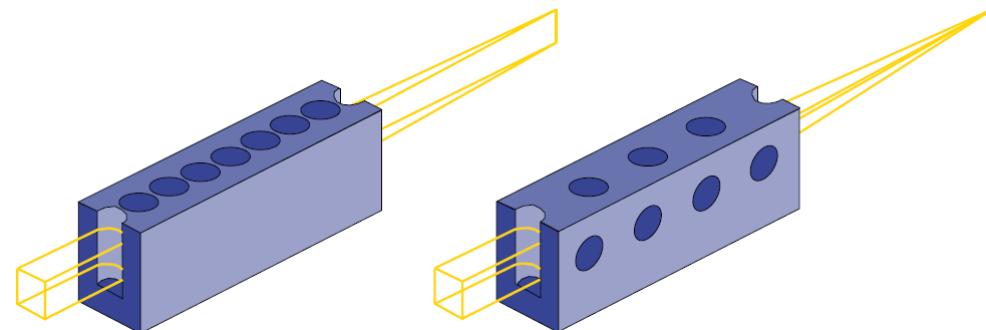
# Focussing mirrors



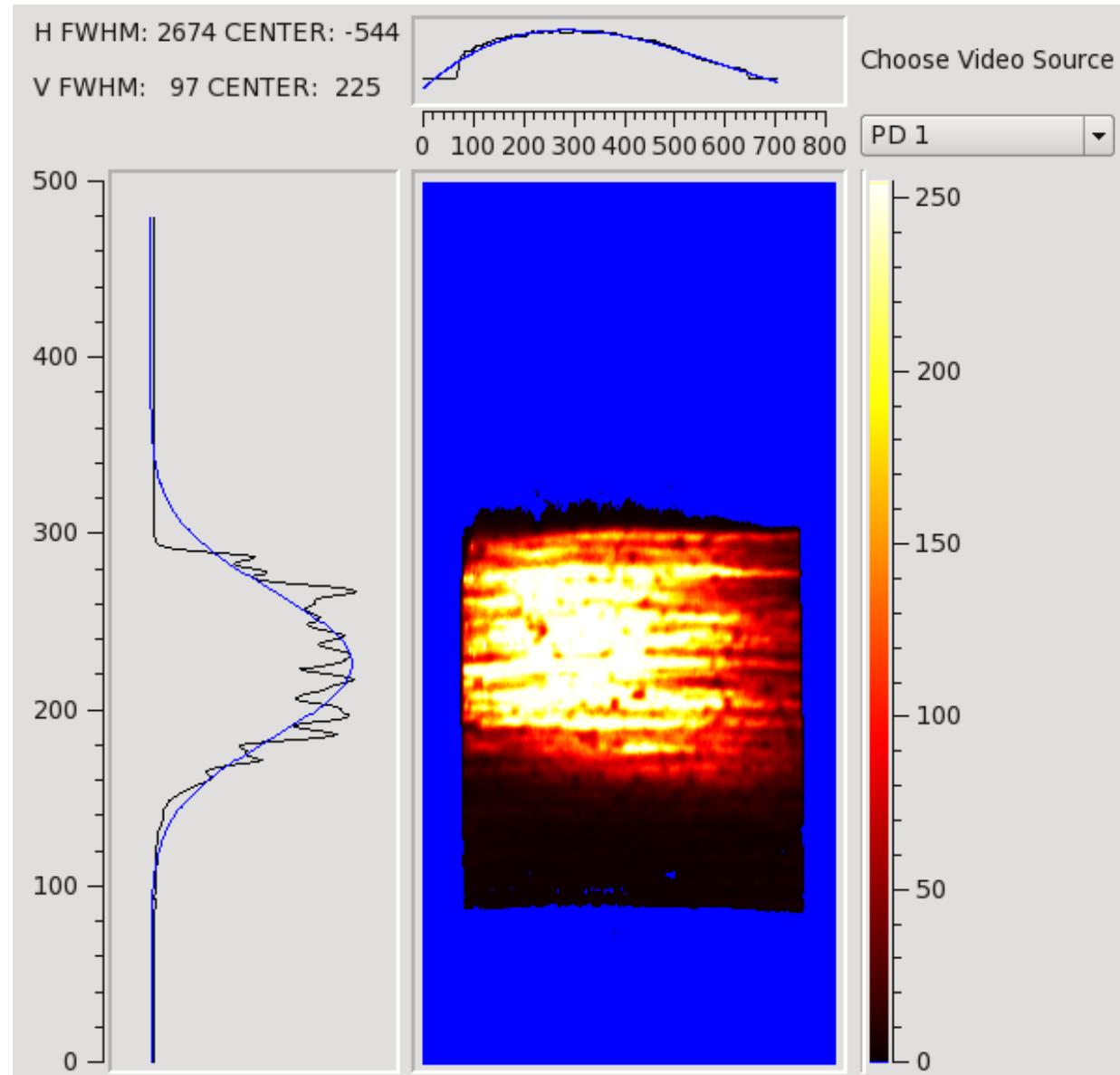
# Focussing



- Glass capillaries
- Compound refractive lenses
- Fresnel Zone plates



# Optical elements



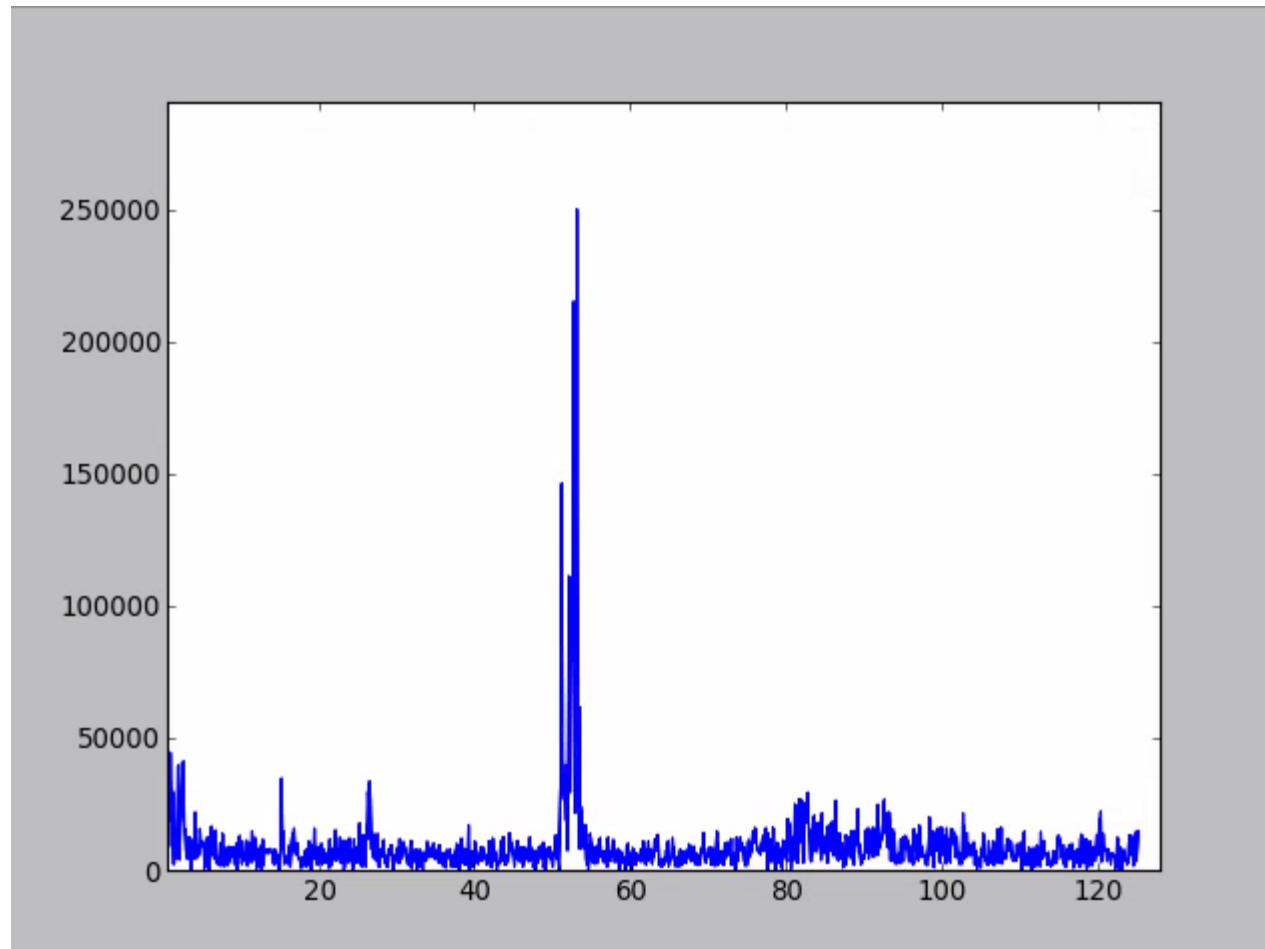
- Wavelengths
- Focusing
- Insertion device
- Mirrors

# Intensity fluctuation



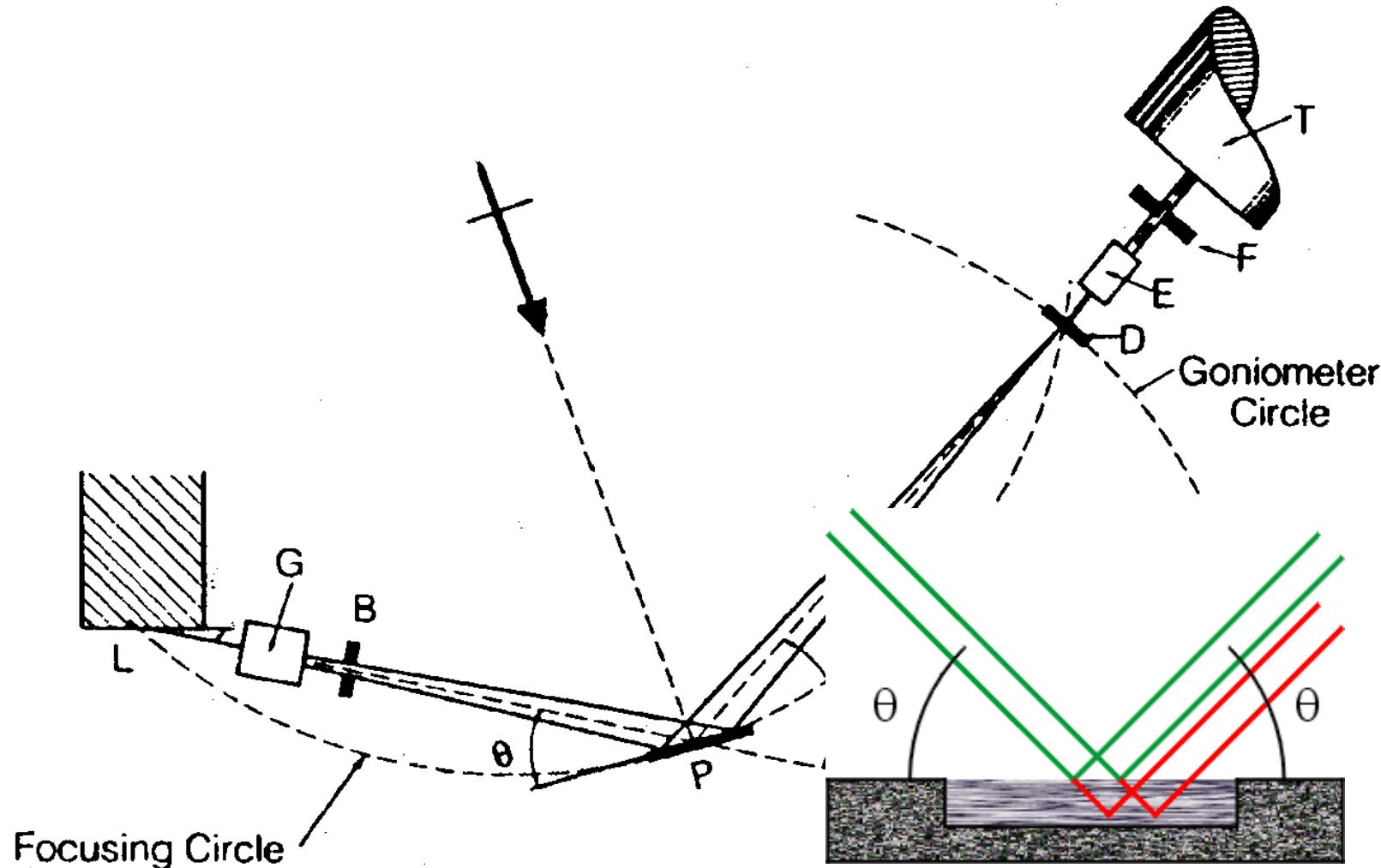
Intensity monitor  
Don't collect at topups

# Beam vibration

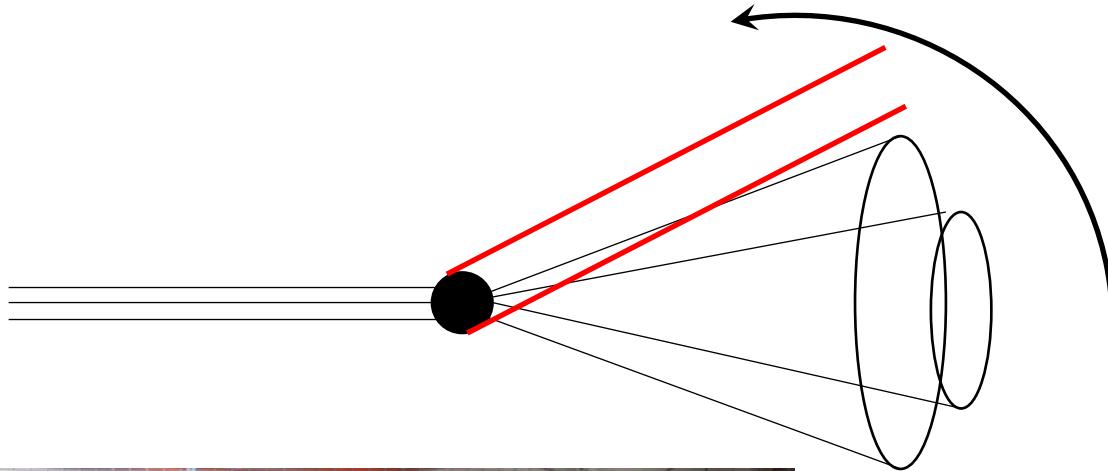


Check your position!

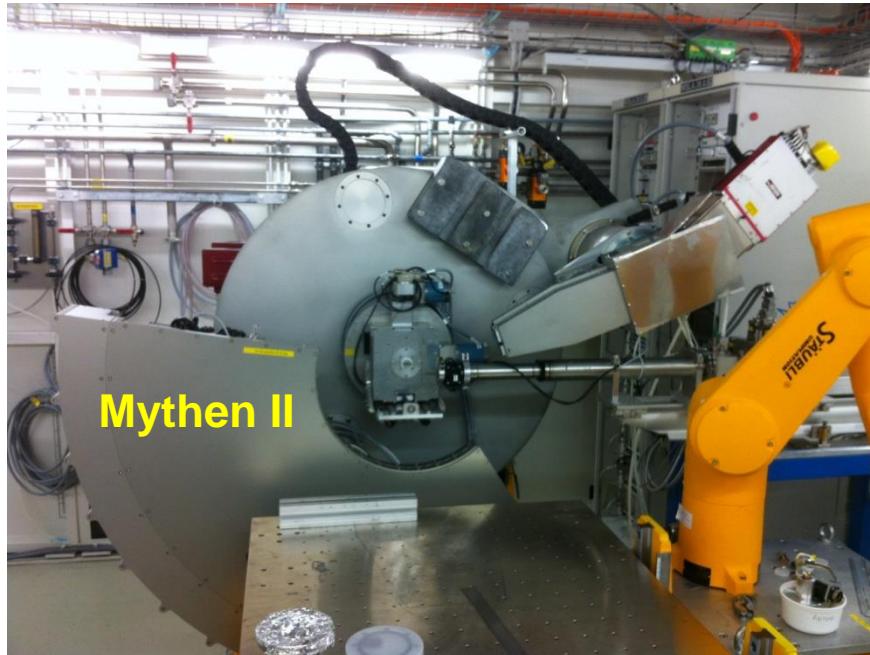
# Bragg-Brentano



# Debye-Scherrer



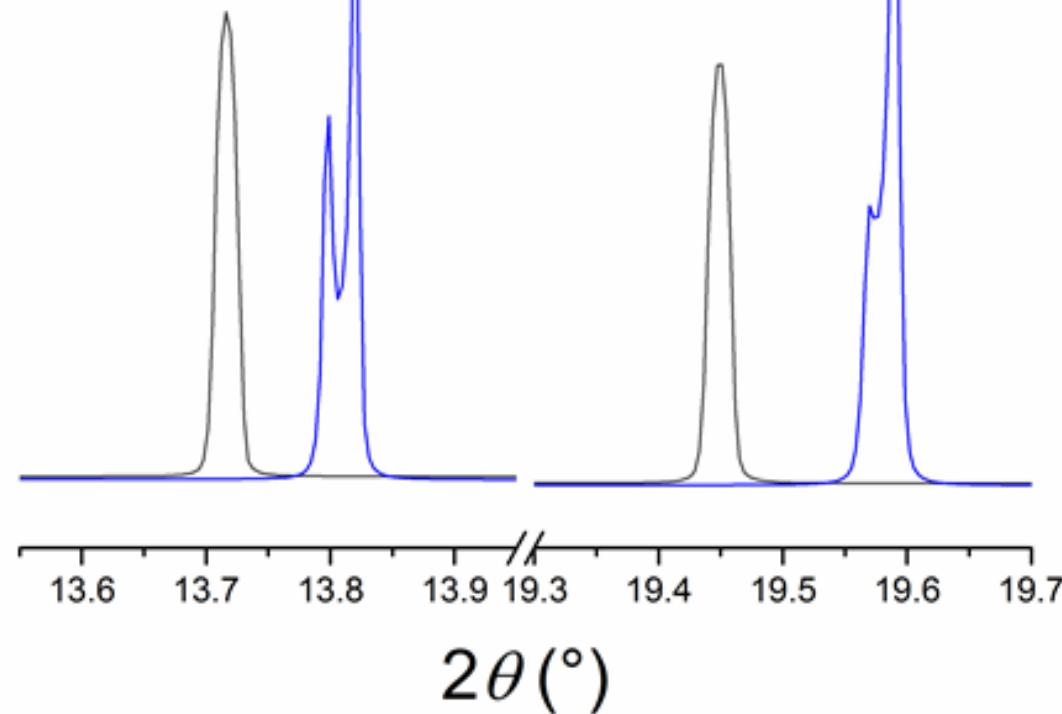
- Smaller sample, easy spinning
- Size matters



# Absorption

12.4 keV

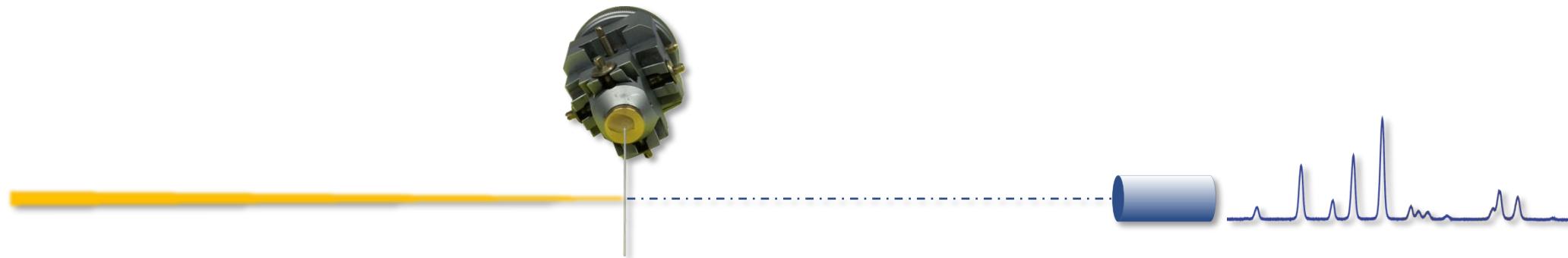
— NAC in 0.3 mm diameter capillary  
—  $\text{LaB}_6$  in 0.3 mm diameter capillary



# PXRD and detectors

Acquisition time  
~ hours

¶e olde method...



# More detectors ...

Multiple single detectors



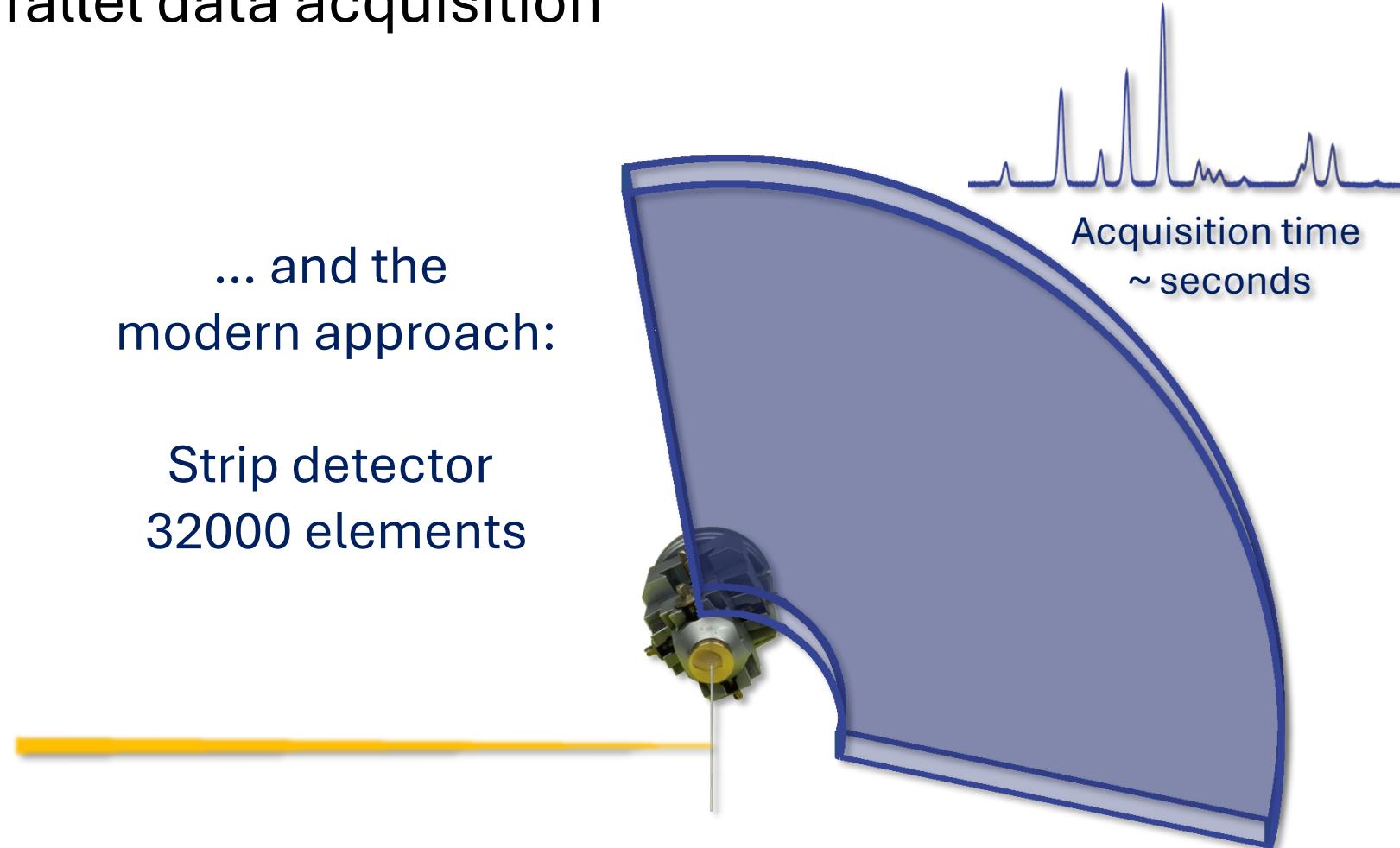
- Position sensitive detectors (Scanning)

# Large stationary PSD

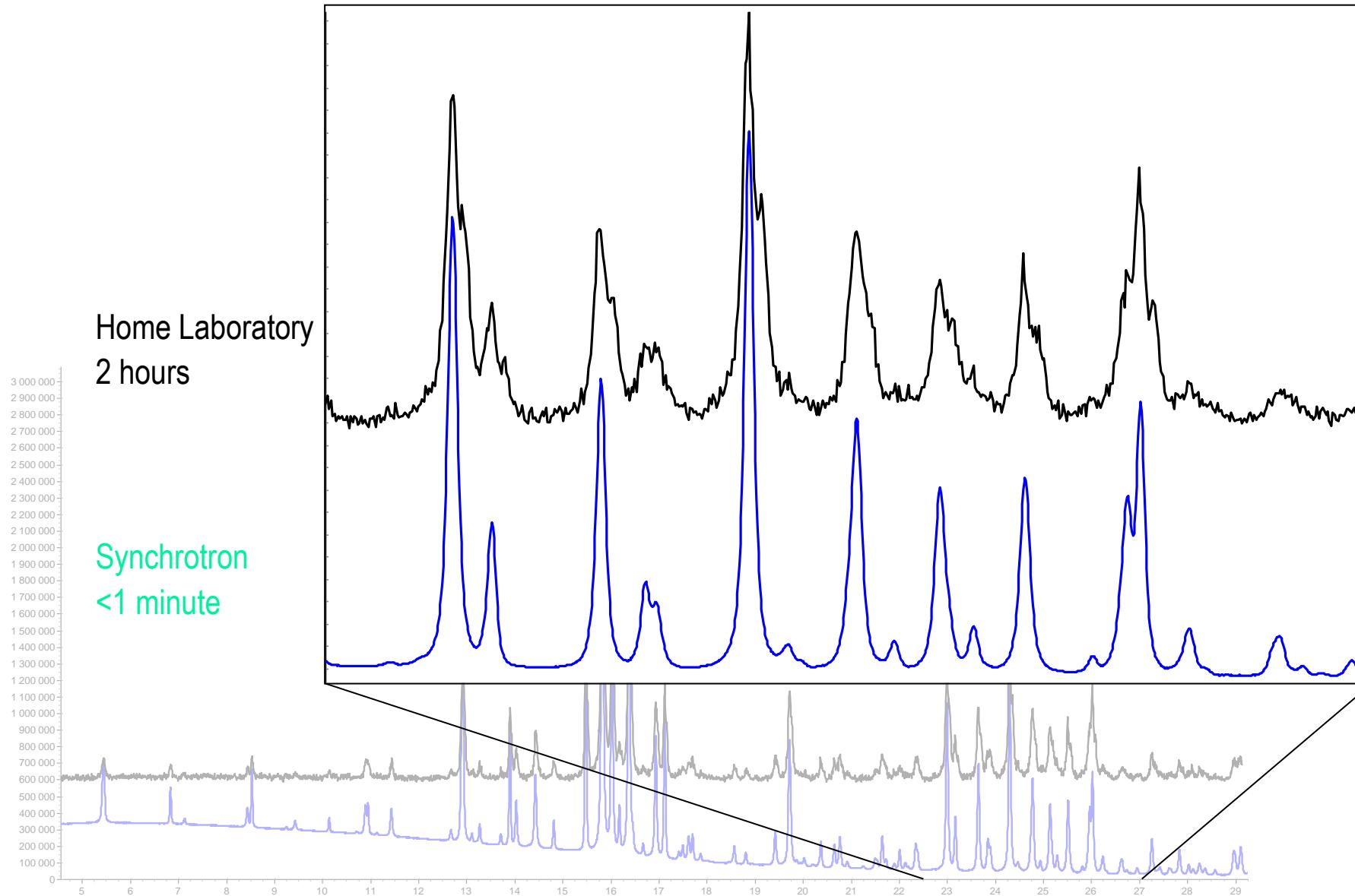
Parallel data acquisition

... and the  
modern approach:

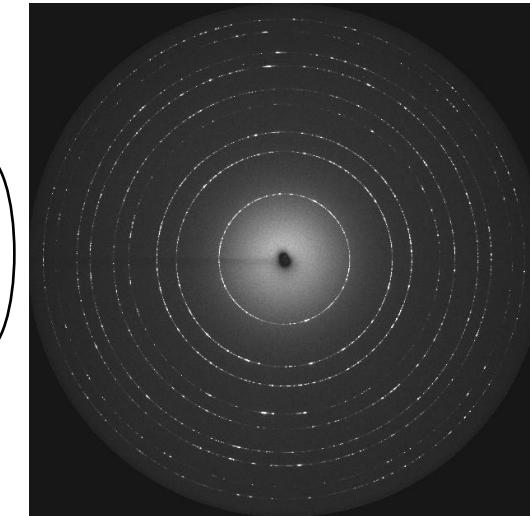
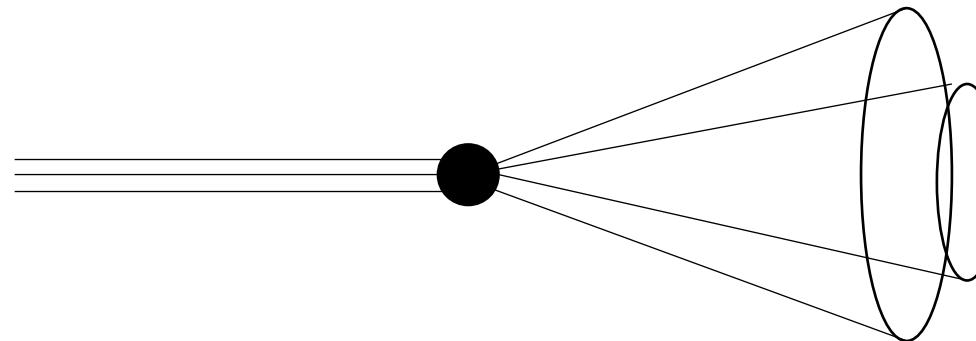
Strip detector  
32000 elements



# Powder diffraction with synchrotron radiation



# With Area detectors

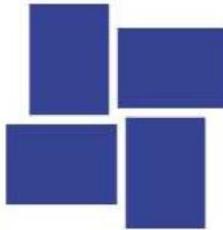


# We only usually take a slice!

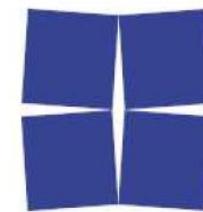
single  
crystal



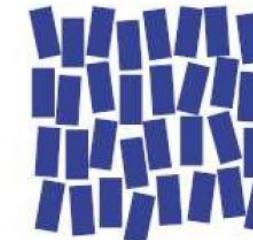
twinned  
crystal



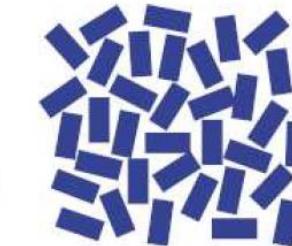
crystal with  
mosaic spread



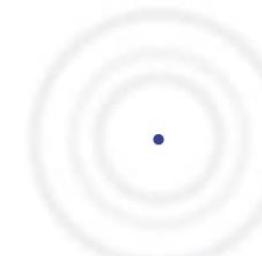
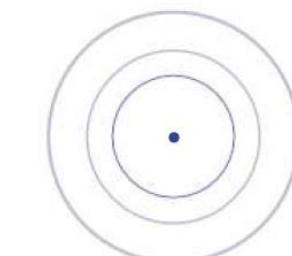
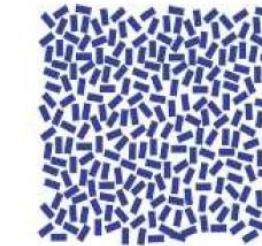
textured  
sample



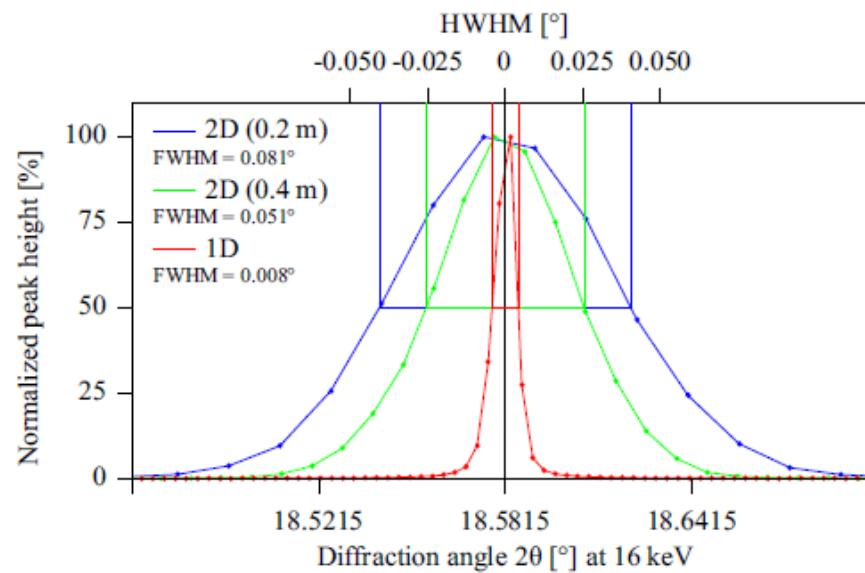
powder  
sample



nanocrystalline  
powder

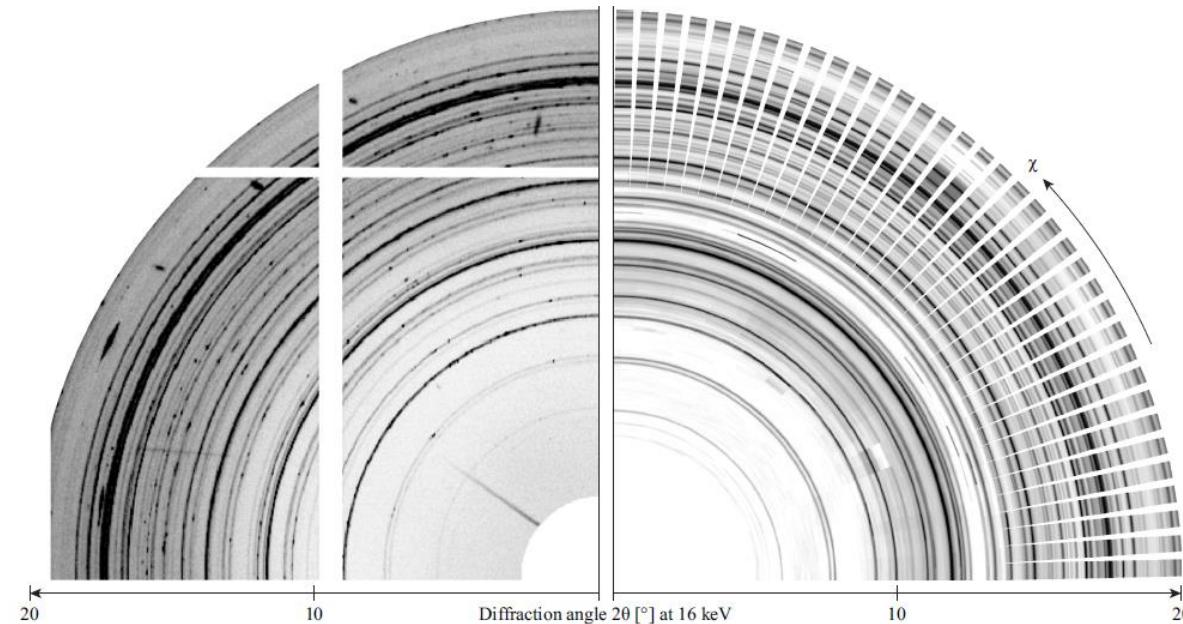


# 1D vs 2D

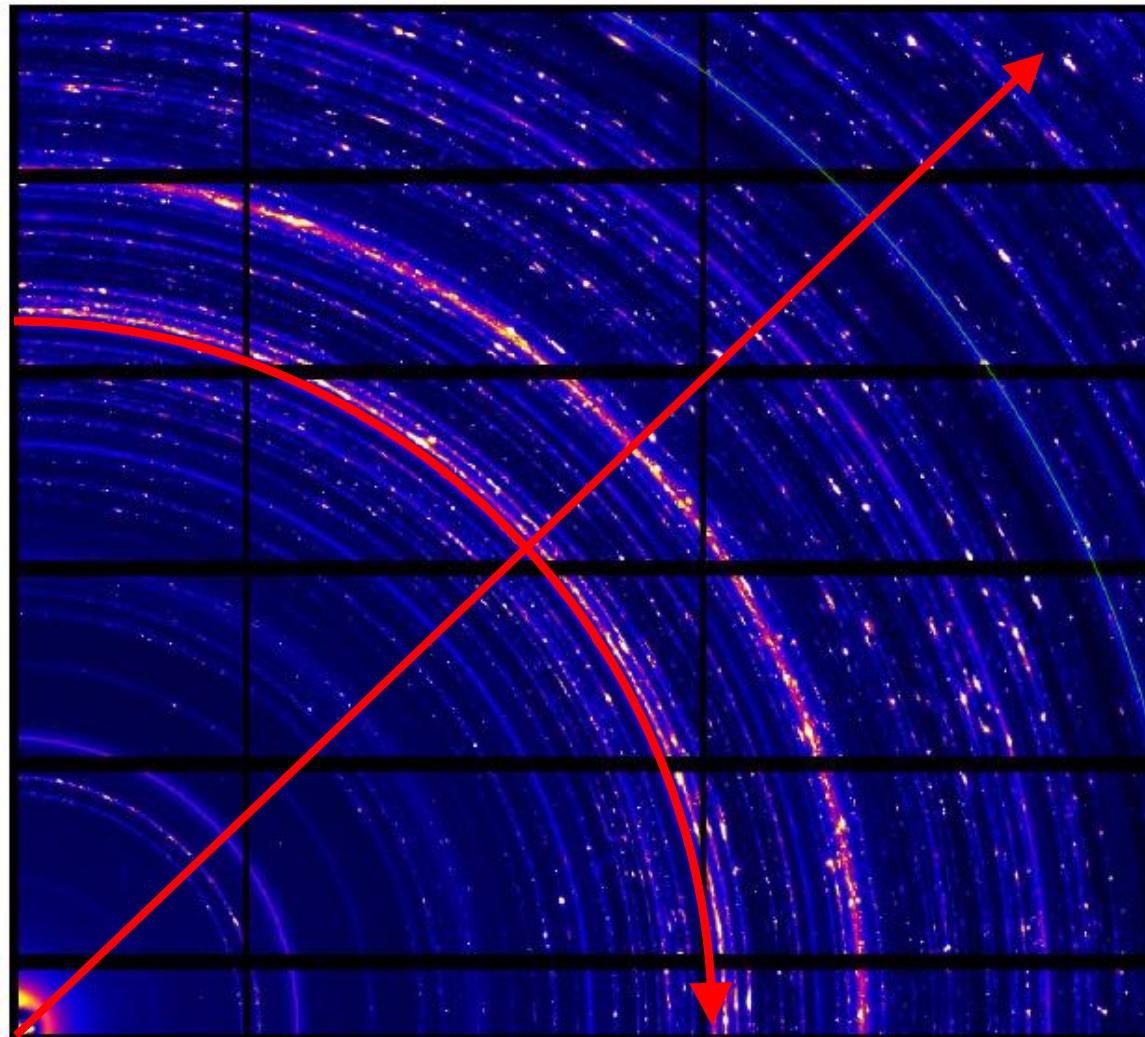


## Resolution

## Statistics



# Non statistical powder

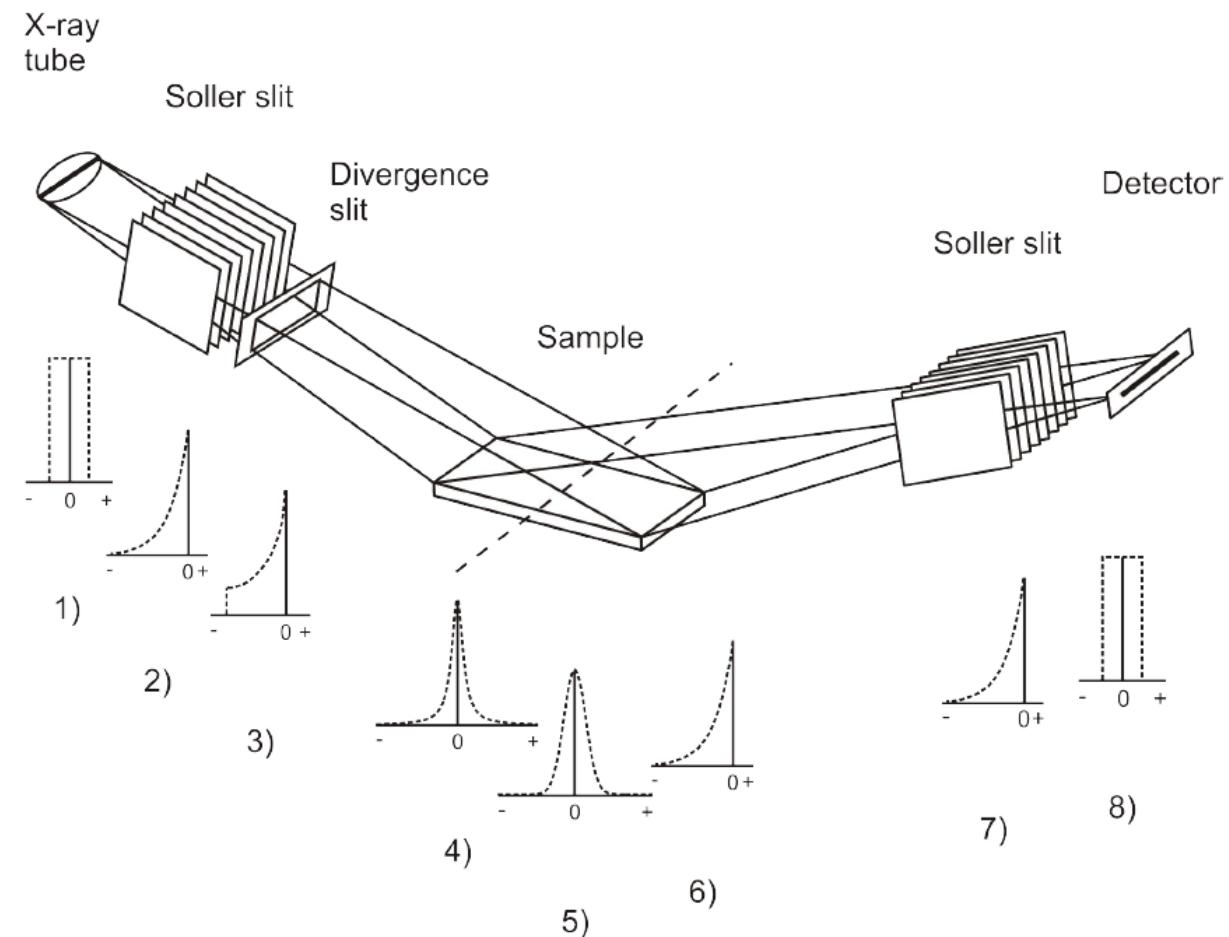


Too few grains due to

- Small amount of sample
- Small amount of a phase in a sample
- Impossibility to grind
- Impossibility to rotate/spin significantly the sample (chambers)
- On purpose oriented grains

# Instrumental Resolution Function

Fundamental Parameters approach, each instrumental contribution is convoluted based on the known instrumental elements and contribution



# Instrumental Resolution Function



Use of a calibrated standard (NIST SRM, CeO<sub>2</sub>, LaB<sub>6</sub>, Si etc.)

- Same exact setup needed if not internal
- Similar packing is external
- Similar absorption
- Similar or slightly extended angular range needed
- Should not contribute to the peak broadening

Fit the instrumental contribution as well as you can (Cauchy, Gaussians, Hats, various combinations, popular is the one by Caglioti, Paoletti, Ricci (1958))

Fix it

Analyse your sample. All remaining broadening comes from it

# Peak broadening – Scherrer's

Exact for monodispersed, strain-free, cubic particles

In 1918 Scherrer devised the following:

$$B(2\theta) = \frac{K\lambda}{L \cos \theta}$$

- B is FWHM at  $2\theta$
- K is 0.94 (for a cube)
- $\lambda$  is the wavelength
- L is the **size**, bingo!

Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen.

Von

P. Scherrer.<sup>1)</sup>

Vorgelegt von P. Debye in der Sitzung vom 26. Juli 1918.

Über die innere Struktur der Kolloidteilchen ist bis jetzt mit Sicherheit nichts bekannt. Es ist daher interessant, typische anorganische und organische Kolloide nach der Methode der regellos orientierten Teilchen<sup>1)</sup> auf ihre Röntgeninterferenzen und damit auf ihren inneren Aufbau zu untersuchen. Es sind dabei von vornherein zwei verschiedene Fälle denkbar.

1. Das einzelne Kolloidteilchen besitzt kristallinische Struktur. Dann haben wir auf unseren Röntgenaufnahmen zahlreiche Interferenzen zu erwarten, die in für das Raumgitter charakteristischer Weise angeordnet sind. Man hat sich natürlich zu überlegen, ob Kriställchen von der Größe von Kolloidteilchen noch Anlaß zu solchen Interferenzen geben können, ob nicht durch die Kleinheit der Teilchen die Erkennung der Kristallstruktur in Frage gestellt wird. Die Theorie gibt uns darüber folgende Aufschlüsse:

a) Die Lage der Interferenzen, die durch eine bestimmte kristallinische Substanz veranlaßt werden, hängt gar nicht von der Größe der verwendeten Einzelkriställchen ab. Sie ist ganz allein bestimmt durch die Art des Raumgitters.

b) Die Breite der Interferenzen hängt eng zusammen mit der Größe der verwendeten Einzelkriställchen, und zwar werden

1) P. Debye u. Scherrer, Phys. Z. 17, 277, 1916.

Bestimmung der Größe und der inneren Struktur von Kolloidteilchen. 99

die Maxima um so breiter, je geringer die Anzahl der Elementarbereiche ist, die das Einzelteilchen umfaßt. Man ist sogar in der Lage durch Messung des Intensitätsverlaufs in den Interferenzen und damit der Breite derselben auf die Größe der verwendeten Kriställchen zu schließen, und bekommt damit, falls man es wirklich mit kristallinischen Teilchen zu tun hat, eine neue Methode zur Bestimmung der Teilchengröße. Die Theorie ergibt für die in bekannter Weise definierte Halbwertsbreite  $h$  des Maximums, das unter dem Winkel  $\vartheta$  gegen den einfallenden Röntgenstrahl auftritt, den Wert:

$$h = 2 \sqrt{\frac{\ln 2}{\pi}} \cdot \frac{\lambda}{A} \cdot \frac{1}{\cos \vartheta/2}.$$

Dabei ist  $\frac{\lambda}{A}$  das Verhältnis der Wellenlänge der benutzten monochromatischen Röntgenstrahlen zur Kantenlänge des als würffelförmig vorausgesetzten Kriställchens.

2. Falls Kolloidteilchen keine kristallinische Struktur aufweisen, haben wir nur ein oder zwei sehr flache Maxima in der Nähe des einfallenden Röntgenstrahles zu erwarten<sup>1)</sup>. Es ist dann schwer, Näheres über die innere Atomanordnung auszusagen.

Ausgehend von diesen theoretischen Überlegungen wurden Experimente angestellt die zu folgenden hauptsächlichen Resultaten führten:

1. Sie zeigten, daß kolloidale Au- und kolloidale Ag-Teilchen kleine Kriställchen darstellen, die genau dasselbe Raumgitter aufweisen wie makroskopische Goldkristalle. Es zeigte sich ferner die Formel für die Winkelabhängigkeit der Halbwertsbreite gut bestätigt und es ergaben sich für die Teilchengrößen Werte, die mit den auf anderen Wegen<sup>2)</sup> (Auszählung mit dem Ultramikroskop und osmotischer Druck) bestimmten Werten sehr gut übereinstimmten. Erwähnenswert ist, daß auch bei allerkleinsten Au-Teilchen, die nur noch 4–5 Elementarbereiche längs einer Würfelkante enthalten, also im Ultramikroskop längst nicht mehr sichtbar sind, das Raumgitter mit seinen charakteristischen Abständen genau erhalten bleibt.

2. Es wurden ferner gealterte Kieselsäure und Zinnsäure-Gele untersucht. Diese beiden vom kolloidchemischen Standpunkt so interessanten Körper zeigten neben den Anzeichen amorpher

100 P. Scherrer, Bestimm. d. Größe u. d. inneren Struktur v. Kolloidteilchen.

Körper intensive kristallinische Interferenzen. Wir haben es bei diesen Substanzen mit Körpern zu tun, die im Begriffe sind zu kristallisieren.

3. Typische organische Kolloide: Eiweiß, Gelatine, Casein, Cellulose, Stärke usw. zeigten alle amorphe Struktur, eine Tatsache die es wahrscheinlich macht, daß diese Kolloidteilchen entweder Einzelmoleküle sind oder daß sie aus regellos nebeneinander gelagerten Molekülen bestehen.

Göttingen, Physikalisches Institut, 26. Juli 1918.

# Peak broadening – Scherrer's

Exact for monodispersed, strain-free, cubic particles

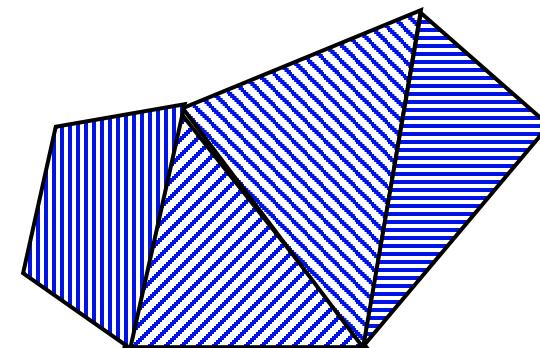
In 1918 Scherrer devised the following:

$$B(2\theta) = \frac{K\lambda}{L \cos \theta}$$

**Size** of what?

- Crystallite (grain) – homogeneous diffracting portion
- Particles – agglomerates of 1 or more crystallites

- B is FWHM at  $2\theta$
- K is 0.94 (for a cube)
- $\lambda$  is the wavelength
- L is the **size**, bingo!



Powder Diffraction is sensitive to crystallites, not particles

# Peak broadening – Scherrer's

Exact for monodispersed, strain-free, cubic particles

In 1918 Scherrer devised the following:

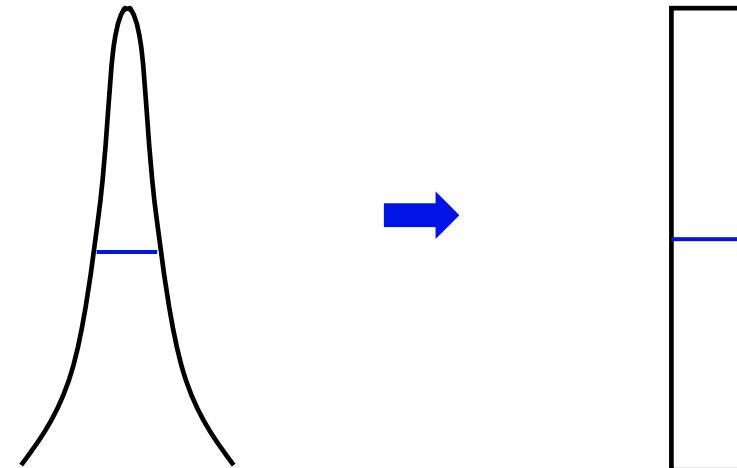
$$B(2\theta) = \frac{K\lambda}{L \cos \theta}$$

Other shaped crystallites may have K values of different values.

It was noticed the Integral Breadth is less sensitive to particle shape and  $K \approx 1$

FWHM

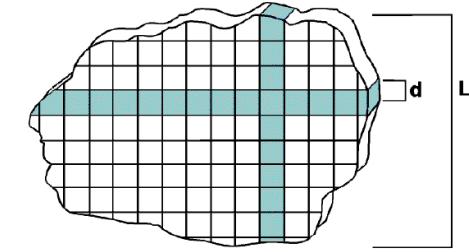
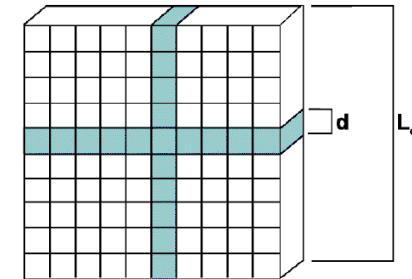
IB: same area, same height  
sensitive to integration



- B is FWHM at  $2\theta$
- K is 0.94 (for a cube)
- $\lambda$  is the wavelength
- L is the **size**, bingo!

# Which size?

- $L_0$  in Scherrer's formula is the edge of the cube
- $L_{vol}$  is the volume weighted mean column length of a crystallite, defined in each direction
- Shape is needed to relate  $L_{vol}$  and  $L_0$
- This is a single value, representing an entire size-distribution ... inherently an approximation and one related to what diffraction 'sees' best. Shape is needed to get real numbers



# Which size?

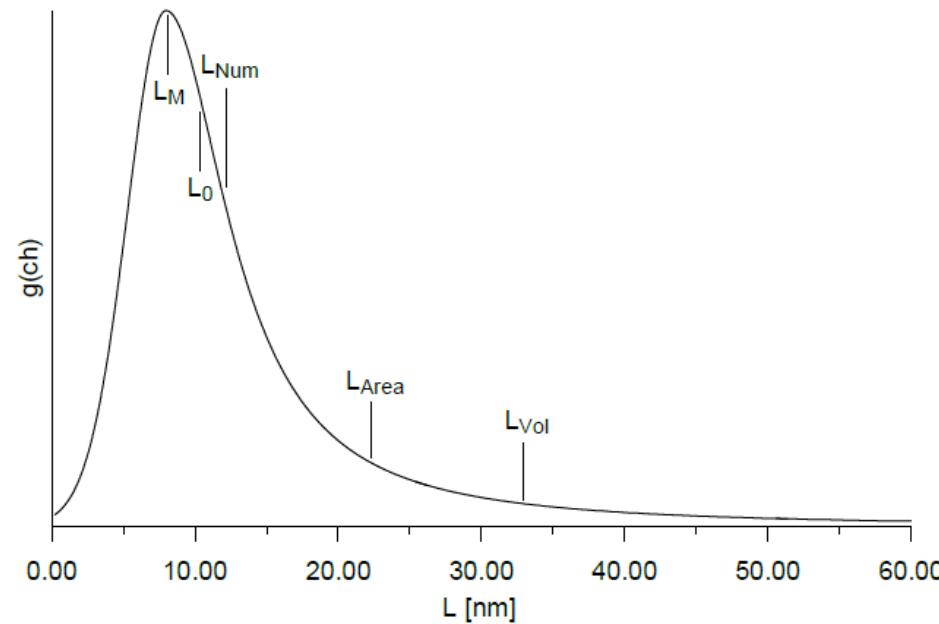
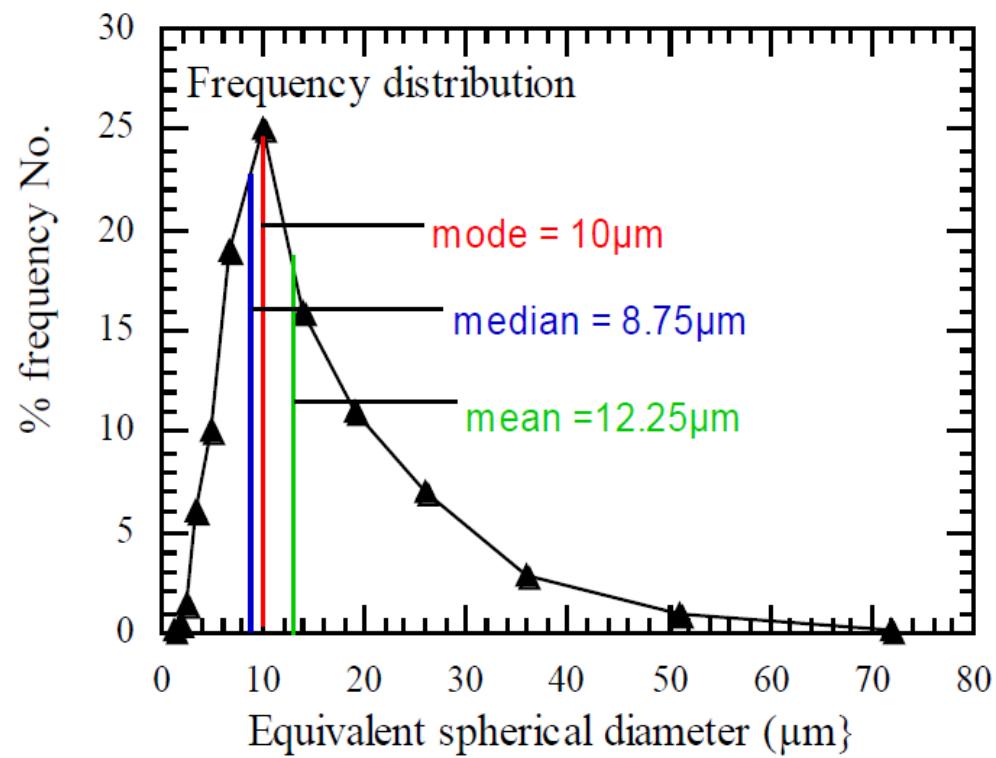
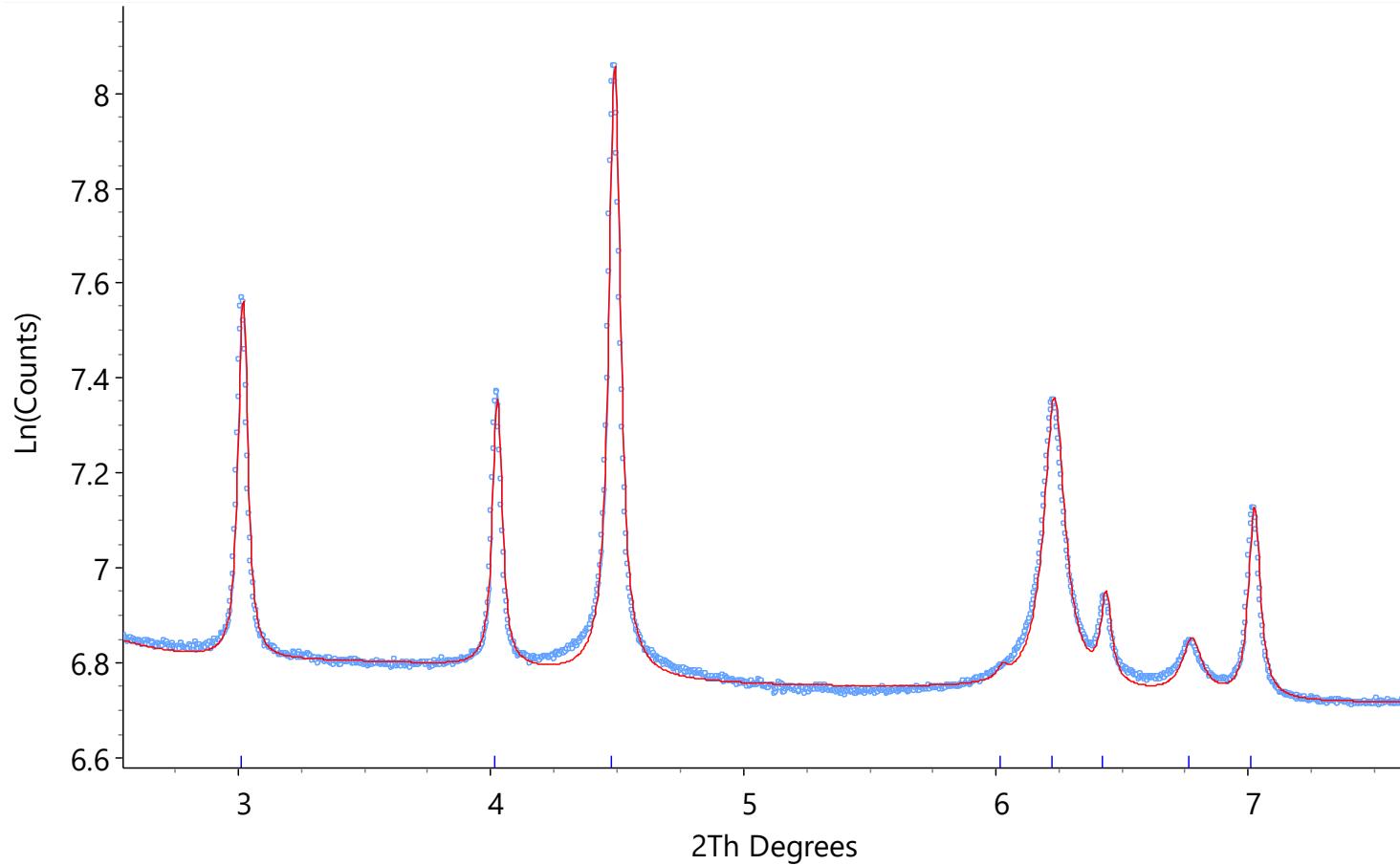


Fig. 7.4: Schematic representation of a column height distribution  $g(ch)$  showing the following characteristic points:

- $L_M$  : mode
- $L_0$  : median
- $L_{\text{Num}}$  : number weighted mean
- $L_{\text{Area}}$  : area weighted mean
- $L_{\text{Vol}}$  : volume weighted mean

# Anisotropic size broadening

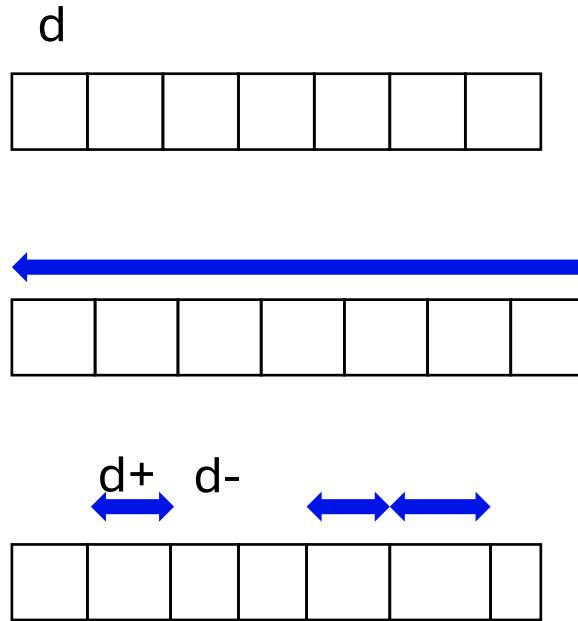


Moreover, anisotropic crystallites lead to anisotropic broadening, in this case the 111 peak is not well fitted

Anisotropic broadening is needed to improve materials understanding

# Broadening – (micro)Strain

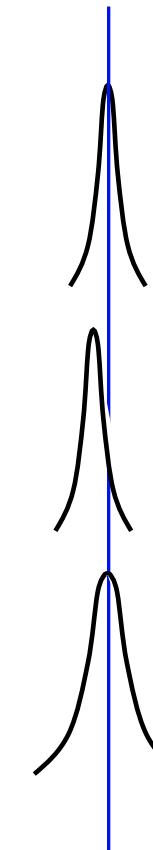
microstrain, often linked to defects, is representative of lattice distribution



Pristine Crystal

Stressed Crystal

Microstrained Crystal



$$B(\theta) = 4\epsilon_0 \tan \theta \quad \epsilon_0 = \Delta d/d$$

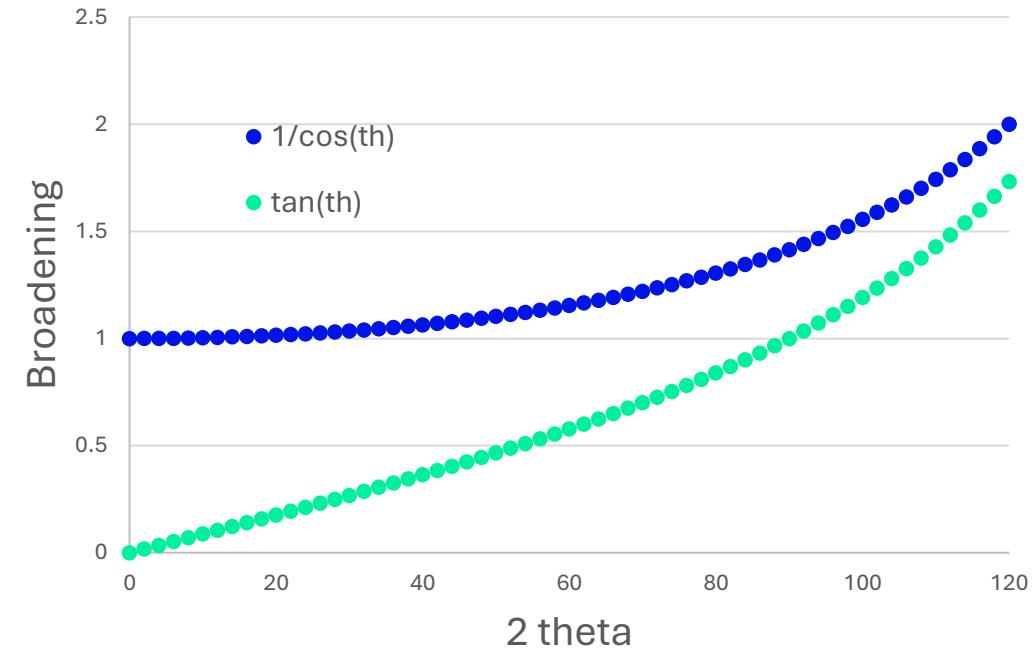
# Broadening sources

Both size and microstrain cause a broadening that grows with angle, but with different dependencies, hence one could differentiate them (in principle ...)

$$B_L(\theta) = K \lambda / L_0 \cos\theta$$

$$B_\varepsilon(\theta) = 4\varepsilon_0 \tan\theta$$

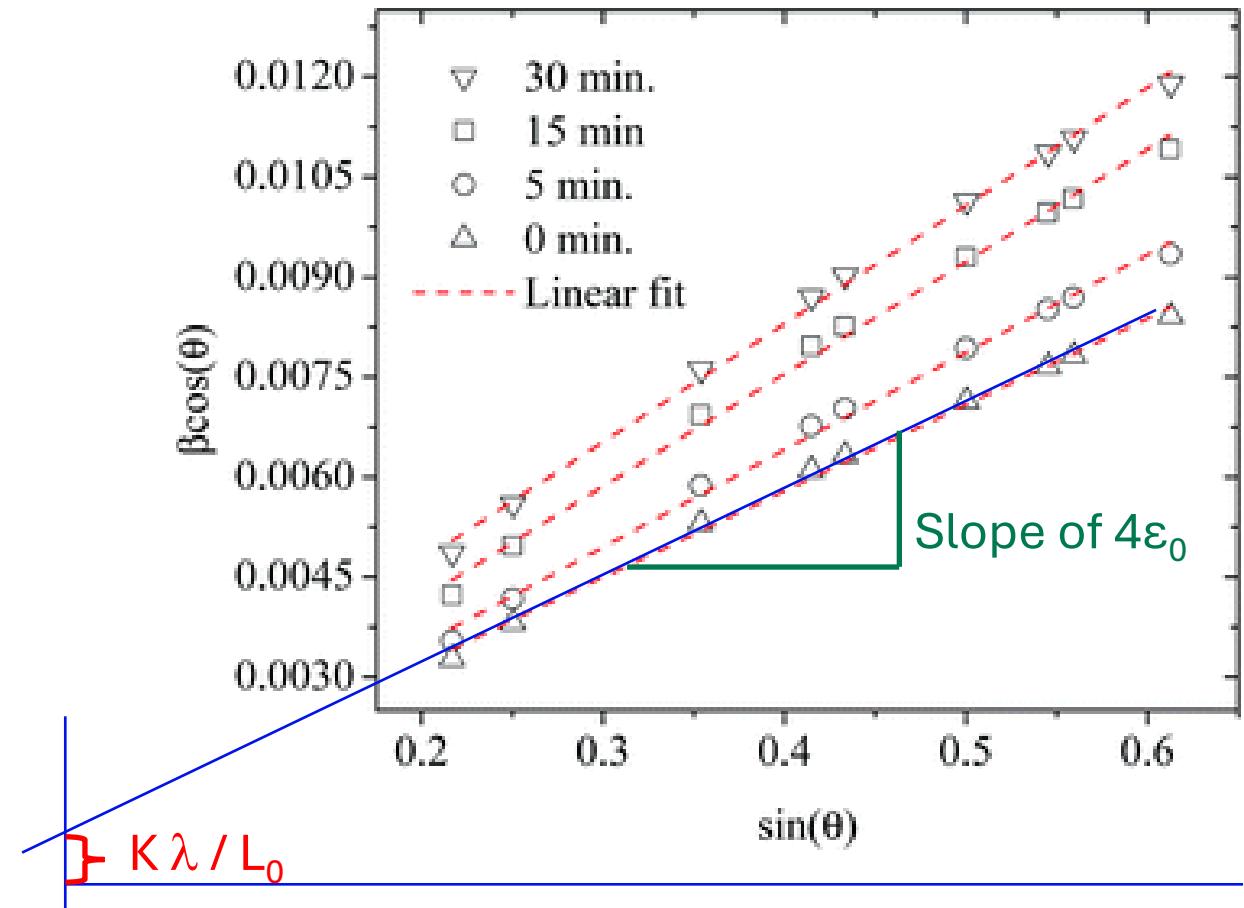
$$B_{\text{tot}}(\theta) \cos\theta = 4\varepsilon_0 \sin\theta + K \lambda / L_0$$



# Williamson Hall plot

$$B_{\text{tot}}(\theta) \cos \theta = 4\epsilon_0 \sin \theta + K \lambda / L_0$$

Things may turn a lot more complicated on less educated samples, with anisotropic broadening etc.



# Microstrain sources

Table 1. The most typical correlations between diffraction peak aberrations, i.e. broadening, shifts or asymmetries, and the different elements of microstructure

Sources of strain	Peak aberrations				
	Peak shift	Peak broadening	Peak asymmetry	Anisotropic peak broadening	Peak shape
Dislocations		+	+	+	+
Stacking faults	+	+	+	+	+
Twinning	+	+	+	+	+
Microstresses		+			
Long-range internal stresses	internal	+		+	
Grain boundaries		+	+		
Sub-boundaries		+	+		
Internal stresses		+			
Coherency strains		+	+	+	
Chemical heterogeneities		+	+	+	
Point defects					+
Precipitates and inclusions				+	+
Crystallite smallness		+		+	+

# Can we get something good from refinements?



Journal of  
Applied  
Crystallography  
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## Size-strain line-broadening analysis of the ceria round-robin sample

D. Balzar,<sup>a,b\*</sup> N. Audebrand,<sup>c</sup> M. R. Daymond,<sup>d</sup> A. Fitch,<sup>e</sup> A. Hewat,<sup>f</sup> J. I. Langford,<sup>g</sup> A. Le Bail,<sup>h</sup> D. Louër,<sup>c</sup> O. Masson,<sup>e</sup> C. N. McCowan,<sup>b</sup> N. C. Popa,<sup>i</sup> P. W. Stephens<sup>j</sup> and B. H. Toby<sup>k</sup>

On a lognormal distribution of practically strain-free spherical CeO<sub>2</sub> particles ...

- Different instruments show similar results
- Different analytical methods show slightly dissimilar results
- Refinements are prone to fail if wrong strain and/or IRF is considered
- Pseudo-Voigt (or more complex) are required for correct interpretation

# Can we get something good from refinements?



## Interlaboratory study on the quantification of calcium phosphate phases by Rietveld refinement

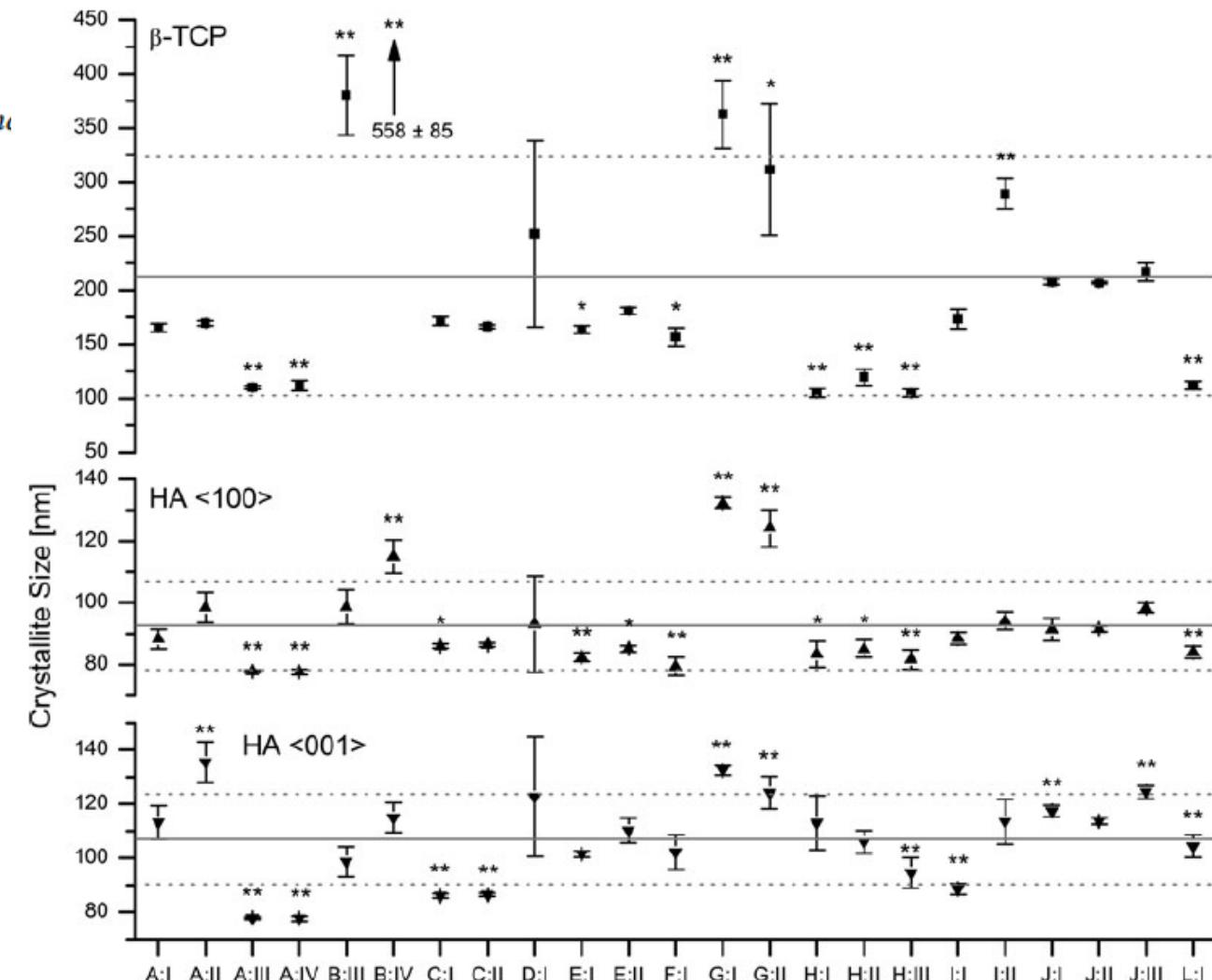
Nicola Döbelin<sup>a)</sup>

*RMS Foundation, Bischmattstrasse 12, 2544 Bettlach, Switzerland*

(Received 25 November 2014; accepted 17 April 2015)

[doi:10.1017/S088571561500038X]

Initially meant for  
quantification but including  
sample size and lattice



# A bit more advanced, WPPM

Acta Crystallographica Section A  
**Foundations of  
Crystallography**  
ISSN 0108-7673

## Whole powder pattern modelling

P. Scardi\* and M. Leoni

Received 16 October 2001  
Accepted 11 December 2001

Dipartimento di Ingegneria dei Materiali, Università di Trento, 38050 Mesiano (TN), Italy.  
Correspondence e-mail: paolo.scardi@ing.unitn.it

Does not compute arbitrary shape functions for peaks but rather analytical contributions based on the different effects of shape and size distribution, dislocations, stacking faults, grain surface relaxation etc.  
Incidentally can also include the structure ...  
As for every refinement, results are as good as the educated assumptions that guide the choice of parameters

# A bit more advanced, WPPM

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## Whole powder pattern modelling

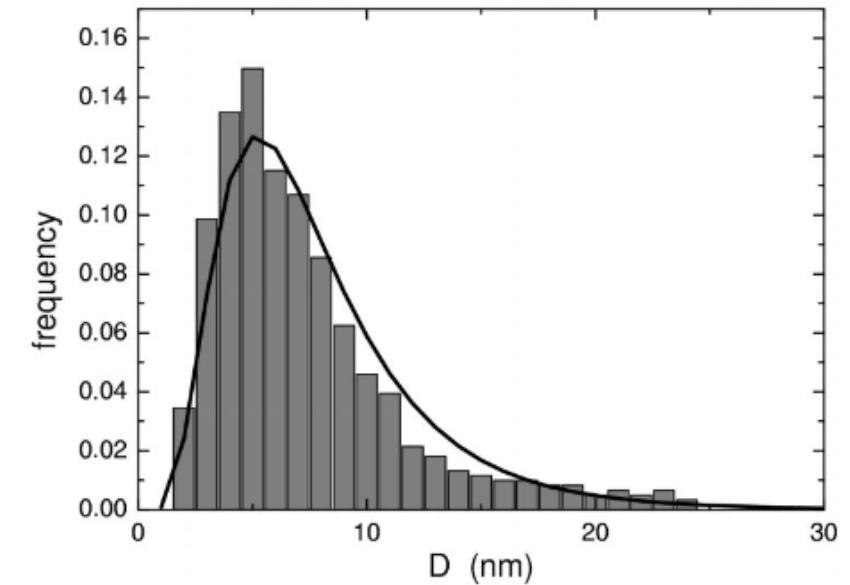
P. Scardi\* and M. Leoni

Dipartimento di Ingegneria dei Materiali, Università di Trento, 38050 Mesiano (TN), Italy.  
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Does not compute arbitrary shape functions for peaks but rather analytical contributions based on the different effects of shape and size distribution, dislocations, stacking faults, grain surface relaxation etc.

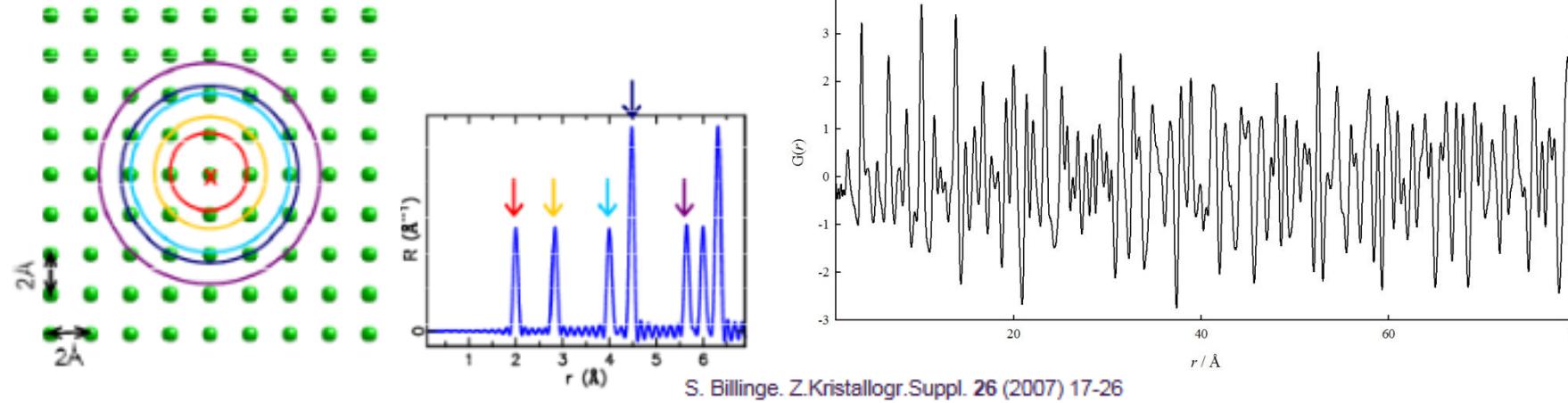
Incidentally can also include the structure ...

As for every refinement, results are as good as the educated assumptions that guide the choice of parameters



**Figure 6**  
Grain-size distribution for sample 96 h: TEM (histogram) and WPPM result (line).

# Total scattering, the Pair Distribution Function



Computed from the FT of the **entire** pattern, represents the probability distribution of finding electron density (i.e. an atom) at a given distance  $r$  from another

Requires high energy to reach very high  $Q$  values as in principle requires ALL diffraction

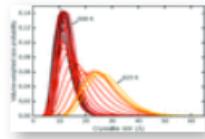
Suitable also for amorphous, liquid and nanocrystalline

# Total scattering, the Pair Distribution Function



JAC RESEARCH PAPERS

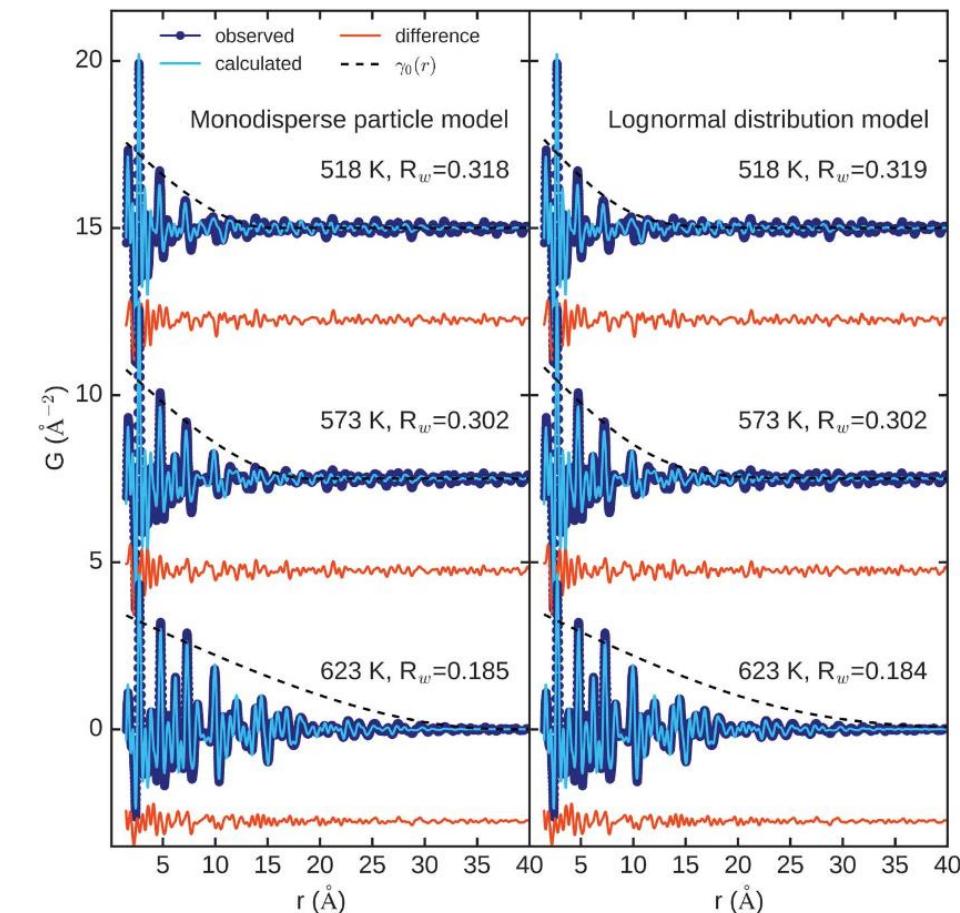
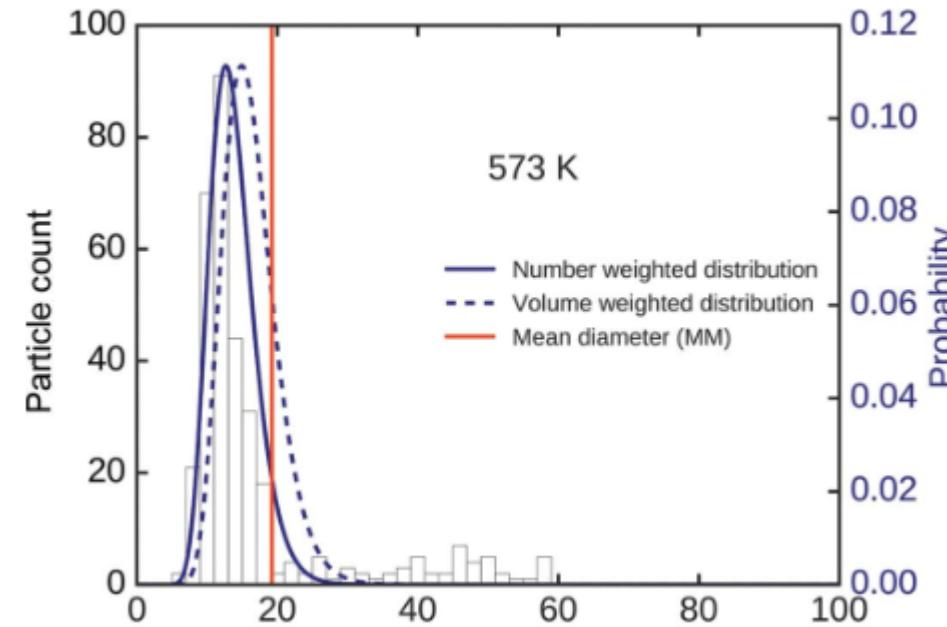
*J. Appl. Cryst.* (2017). **50**, 741-748  
<https://doi.org/10.1107/S1600576717003715>  
Cited by 37



## Modelling and validation of particle size distributions of supported nanoparticles using the pair distribution function technique

L. Gamez-Mendoza<sup>1</sup>, M. W. Terban<sup>1</sup>, S. J. L. Billinge<sup>1</sup> and M. Martinez-Inesta<sup>2</sup>

A monodispersed and a Lognormal model were fitted to the data



# The Debye Scherrer Equation

- Calculates the intensity at a given  $q$  as the sum of all pairwise contributions from atom pairs
- Same approach as PDF but works in reciprocal space and describes analytically (does not need) the total wide-angle scattering
- Requires a sensible model
- Computational wise choices to be made, works better for NP as less atoms!
- Can incorporate naturally size, shape, defects etc.

$$I(q) = \sum_{i=1}^N \sum_{j=1}^N f_i f_j \frac{\sin(qr_{ij})}{qr_{ij}}$$

# The Debye Scherrer Equation

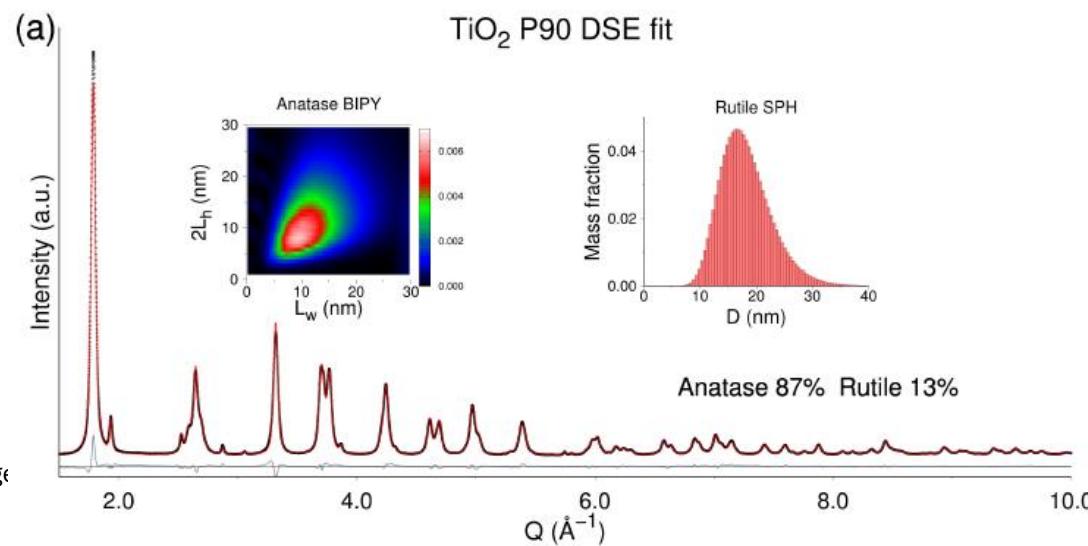


Article

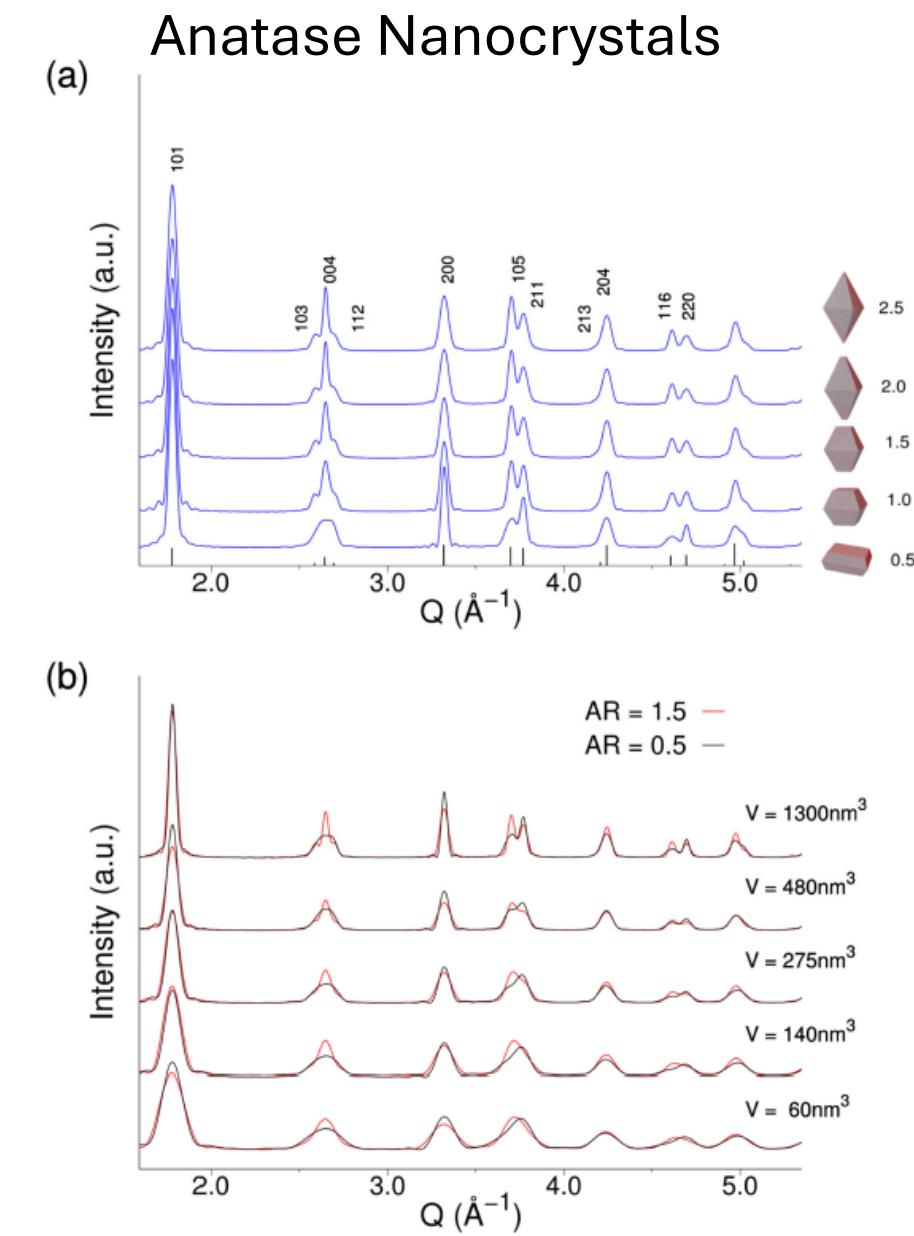
## Structure, Morphology, and Faceting of $\text{TiO}_2$ Photocatalysts by the Debye Scattering Equation Method. The P25 and P90 Cases of Study

Federica Bertolotti <sup>1,\*</sup>, Anna Vivani <sup>1</sup>, Daniele Moscheni <sup>1</sup>, Fabio Ferri <sup>1</sup>, Antonio Cervellino <sup>2</sup>, Norberto Masciocchi <sup>1,\*</sup> and Antonietta Guagliardi <sup>3,\*</sup>

Refinement on a commercial sample of a bivariate population of bipyramidal shapes



Page



# See you at SLS-2!



## Powder Diffraction School - Modern Syncrotron Methods

MSE-663 / 2 credits

**Teacher(s):** Casati Nicola, Testino Andrea, Van Petegem Steven, Various lecturers

**Language:** English

**Remark:** Next time: 2025

**Frequency**

Every 2 years

[Download the coursebook \(PDF\)](#)

### In the programs

**Materials Science and Engineering** ▲  
2024-2025 Doctoral School

- **Number of places:** 40
- **Exam form:** Oral (session free)
- **Subject examined:** Powder Diffraction School - Modern Syncrotron Methods
- **Courses:** 23 Hour(s)
- **Exercises:** 9 Hour(s)
- **TP:** 2 Hour(s)
- **Type:** optional

# What's a refinement?

You have data

Criteria of fit	Definition
"R-pattern", $R_p$	$R_p = \frac{\sum  Y_{o,m} - Y_{c,m} }{\sum Y_{o,m}}$
"R-pattern", $R_p'$ (background corrected)	$R_p' = \frac{\sum  Y_{o,m} - Y_{c,m} }{\sum  Y_{o,m} - Bkg_m }$
"R-weighted pattern", $R_{wp}$	$R_{wp} = \sqrt{\frac{\sum w_m (Y_{o,m} - Y_{c,m})^2}{\sum w_m Y_{o,m}^2}}$
"R-weighted pattern", $R_{wp}'$ (background corrected)	$R_{wp}' = \sqrt{\frac{\sum w_m (Y_{o,m} - Y_{c,m})^2}{\sum w_m (Y_{o,m} - Bkg_m)^2}}$
"R-expected", $R_{exp}$	$R_{exp} = \sqrt{\frac{M - P}{\sum w_m Y_{o,m}^2}}$
"R-expected", $R_{exp}'$ (background corrected)	$R_{exp}' = \sqrt{\frac{M - P}{\sum w_m (Y_{o,m} - Bkg_m)^2}}$
"Goodness of fit", GOF	$GOF = chi = \frac{R_{wp}}{R_{exp}} = \sqrt{\frac{\sum w_m (Y_{o,m} - Y_{c,m})^2}{M - P}}$
"R-Bragg", $R_B$	$R_B = \frac{\sum  I_{o^n,k} - I_{c,k} }{\sum I_{o^n,k}}$

